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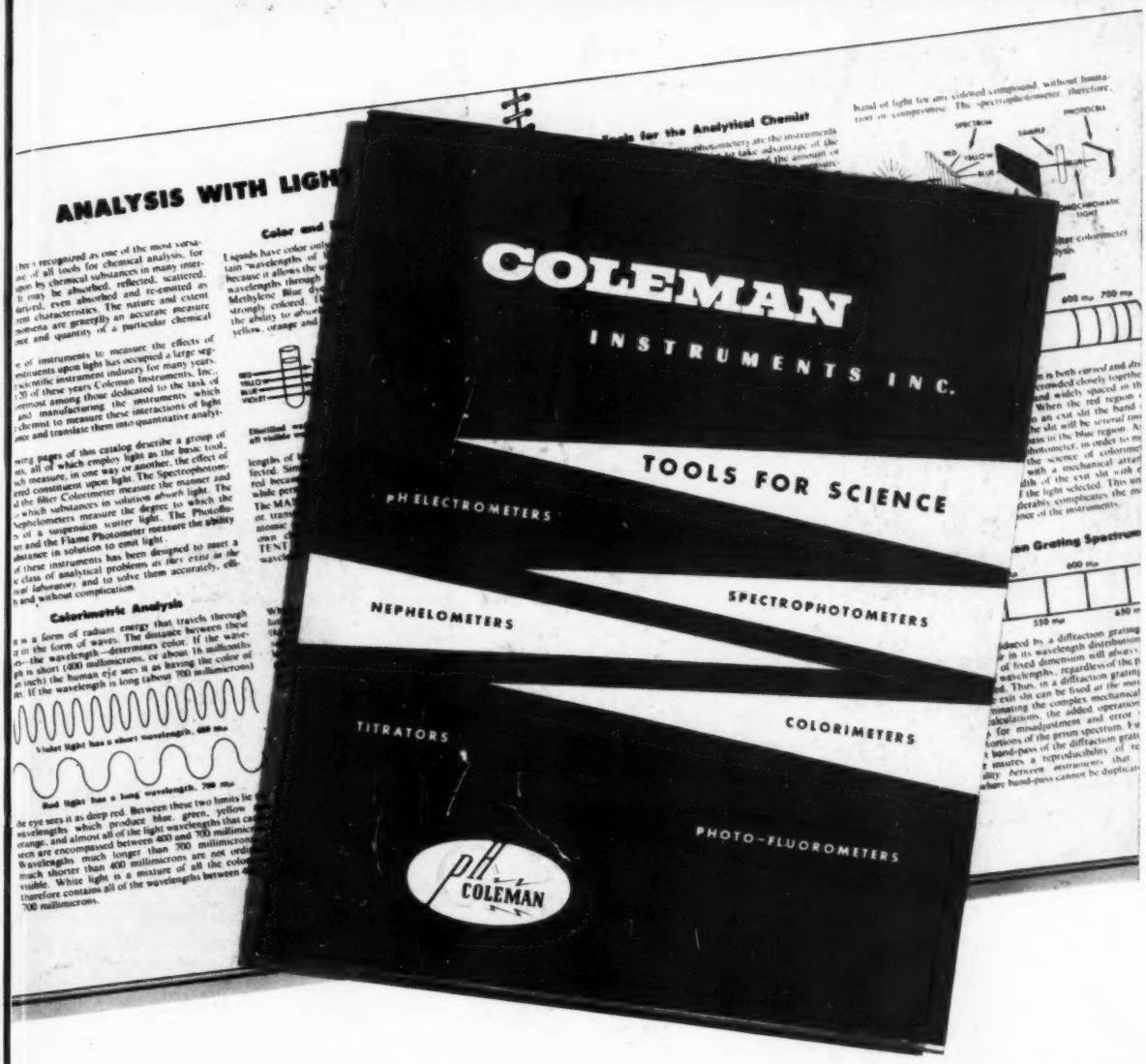
# CHEMICAL EDUCATION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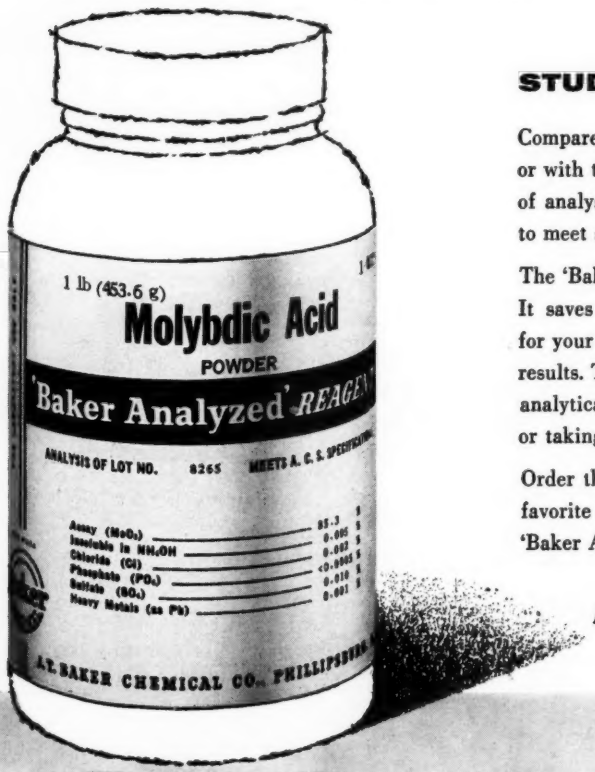


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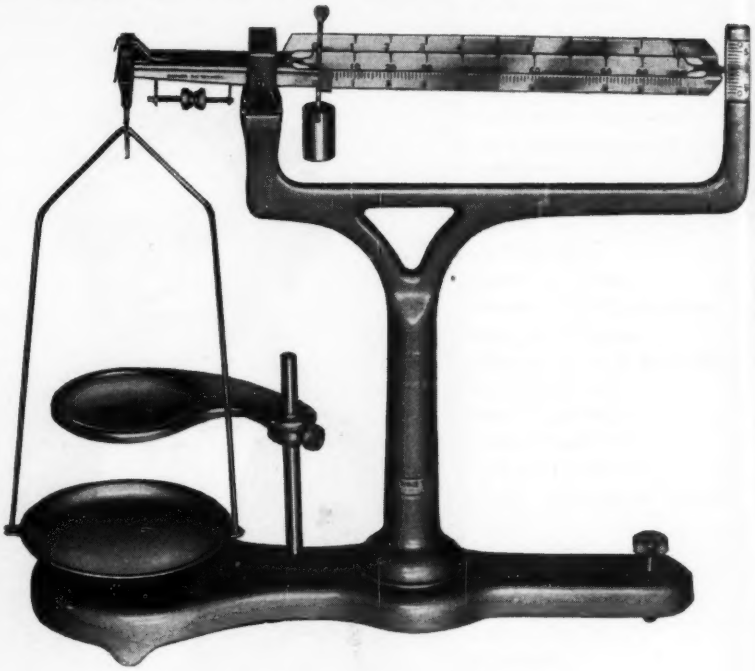

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# Editor's Outlook

DON'T we all enjoy seeing others struggle with the same troubles we have? We in this country are not alone in facing a serious shortage of science teachers. If it is any consolation, our British cousins are in the same boat. Their situation has brought forth a report from an investigating committee appointed by the Federation of British Industries. It must indeed be important, to have agitated such a strongly established agency as the F. B. I.

While their present shortage of science teachers is disturbing, it will inevitably get worse in the next five or six years until, by 1960, an estimated 2000 will be needed. Unfortunately, furthermore, the quality of science teachers has declined, as well as the quantity, for as the available numbers become less it becomes necessary to lower the standards of preparation and ability.

The committee has not beaten around the bush while trying to find reasons for the shortage. To be sure, there has been a decline in the prestige of teaching as a career, and the glamorous appeal of scientific research has attracted many young science graduates who might otherwise have become teachers. But the main trouble is a simple question of pay, salary, emoluments, or financial returns. The prospect is grim when the young graduate views the beginning salaries of science teachers, but it becomes positively discouraging when he compares the salaries of older teachers with those of older scientists in industry or government service.

The F. B. I. committee does not hesitate to recommend raising teachers' salaries, indeed by more than 50 per cent. The present maximum for science teachers is said to be £941; it is suggested that this be raised to £1500. What this means in terms of our own pay scale is of course not determined by merely multiplying by the rate of dollar exchange, but the increase is a very substantial one and might indeed go far toward solving the problem.

It is hardly to be expected that the British financial guardians will be any less reluctant than our own to loosen the purse strings, but the committee report makes the consequences clear if they *don't*. The bill will be in the neighborhood of £1,500,000, but the alternative is the likely drying up of the source of scientific manpower, and disaster for British industry. Furthermore, this sum of money takes into account only the science teachers and not the repercussions on teachers in other fields, who will—understandably—expect a betterment in their own lots if their scientific colleagues get encouragement.

Another interesting point was brought out. Many young graduates have been led into research, both pure and applied, by its stimulating appeal, only to find later on that they were not well adapted or equipped to meet its rigorous demands. But once having started they were unable, because of the discrepancy in salary, to turn to teaching, for which they might be better suited. This at the same time deprived the schools of teachers and weakened the research institutions.

The committee also had something to say about the subject of military deferment. While recognizing the thorny nature of this question, it nevertheless believed that there would have to be some sort of relaxation in the military service requirements for teachers and those preparing for teaching. The British seem to be more realistic than we are in viewing the matter of service in the national interest.

All this has a very familiar ring to those of us who have considered the same problem in our country. Practically every item and conclusion, from the money figures to the urgency of the situation, can be translated into American terms by multiplying by some factor, $n$, of rather large magnitude. (Since 1950, 53 per cent decline in the number of science teachers trained and certified!) Amidst the welter of conflicting interests which seem to be plaguing us, this is one matter upon which our two countries can see eye to eye.

American industry is also aware of the seriousness of this problem and would probably respond vigorously to any suitable plan to meet it. We are coming to see clearly that the science teachers in our schools are the breeders of scientific manpower, which in turn lays the golden eggs for industry. Some of this gold *must* find its way back to the teacher. Surely, in as complicated an economic system as ours, a way can be found to make this simple transfer of funds.

# THEORETICAL CHEMISTRY IN RUSSIA[1]

**I. MOYER HUNSBERGER**
Antioch College, Yellow Springs, Ohio

THE "Iron Curtain" between Russia and the West, coupled with the inability of most Western scientists to read Russian, greatly hampers the Western world in keeping abreast of contemporary Russian science. This situation is aggravated by the recent elimination from Russian journals of non-Russian summaries of technical articles. With respect to review or descriptive scientific articles the situation is even more unfortunate, because English-language abstracts of such articles are extremely brief, often consisting of little more than the authors and titles. All these reasons conspire to render the Western scientific world slow in becoming aware in any detail of the recent Russian criticisms of the resonance theory, of the simultaneous virtual deification of the early Russian chemist, A. M. Butlerov, and of Chelintsev's "New Structural Theory" (which apparently is the lone Russian attempt to produce a theory to replace resonance). Although what apparently was the initial article on the first two of these topics was published in Russia in 1949 (*1*), the resulting controversy was not featured in *Chemical and Engineering News* until late in 1951 (*2*).

Apparently nothing has been published in the English-language scientific literature purporting to examine critically the validity of the Russian claims concerning the above topics, despite the profusion of Russian papers on these subjects since 1949.[2] Undoubtedly the most important reasons for this Western silence are the absence of scientific validity in the Russian criticisms of resonance, the extremely obvious exaggeration of Butlerov's contributions to organic chemistry, and the entire lack of scientific worth in Chelintsev's "New Structural Theory." The large majority of Russian papers on these subjects contains torrents of invective against Western science, apparently arising from the chauvinistic idea that the resonance theory of Linus Pauling opposes the tenets of dialectical materialism and therefore must be rejected. The intensity and crudeness of this invective appear to be without parallel in the annals of chemistry; for this reason it should be publicized. That these ideological arguments have appeared in the most respected Russian journals also should be emphasized.

A less than intensive acquaintance with resonance theory might lead chemists to suspect that the Russian arguments suffer from nothing worse than highly emotional language and actually contain a core of scientific validity.[3] This possibility is even more likely in the case of the lay public. In this article, Russian criticisms of resonance and Russian claims concerning Butlerov will be subjected to critical analysis. The "flavor" of the Russian articles will be shown by direct quotations. If professional readers can agree with the author's analysis, it is hoped that their conclusions will be communicated to the lay public. It is the author's firm conviction that chemists can thereby be of great service in a controversy about which a lay person is to a large extent aware but about which it would otherwise be very difficult for him to reach an informed decision. An even longer-range object of this paper is to present factual information which, it is to be hoped, will assist in an accurate estimation of the results to be expected if the Russians' chauvinistic, ideological approach to scientific theories spreads any further than it has already.[4]

The attention of the Western world was attracted to the nature of Russian claims concerning resonance and concerning Butlerov by the publication early in 1952 of English translations of two articles (*1*, *6*), both of which were representative of Russian views and one of which (*6*) was an official report of the Commission of the Institute of Organic Chemistry of the Academy of Sciences, U. S. S. R. In preparing the present paper the author has carefully studied English translations of eighteen Russian articles (*1*, *6*, *7–22*)[5] (comprising about 250 journal pages), which appeared between 1949 and 1952 in various journals.[6]

[1] Parts of this paper were presented in lectures to the Antioch Student Affiliate Chapter of the American Chemical Society, March, 1952, and February, 1954.

[2] Jensen's paper (*3*) unfortunately has not been available to the author in complete English translation. However, the English summary accompanying this article indicates it to contain a fair evaluation of the Russian claims concerning Butlerov's contributions to organic chemistry.

[3] G. M. Kosolapoff's recent letter (*Chem. Eng. News*, **30**, 2475 (1952)), suggesting that the Russian criticisms of resonance theory are at least partly valid, was prompted by a misunderstanding of the content of the theory. This misunderstanding was promptly clarified by G. W. Wheland (*Chem. Eng. News*, **30**, 3160 (1952)).

[4] The sustained controversy in genetics and its recent denouement (T. D. Lysenko's apparent decline in influence) are too well known to require detailed comment. A similar ideological controversy in Russian theoretical physics recently was reviewed (*4*). A general review on various aspects of Soviet science also was published recently (*5*).

[5] References *7–22* were obtained in English translation from the Consultants Bureau, 152 W. 42nd St., New York 18, New York, and were paid for out of a grant of $2500 awarded to the Antioch Chemistry Department by E. I. du Pont de Nemours for excellence in the teaching of chemistry.

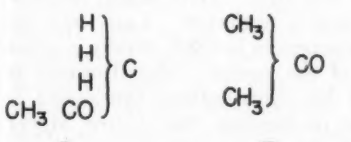
[6] It is hoped that in the near future funds will become available to obtain English translations of additional articles (listed as references *23–35* for bibliographic purposes) pertaining to the subject of the present paper.

## ORGANIC STRUCTURAL THEORY PRIOR TO 1860

A discussion of Butlerov's contributions to organic chemistry can perhaps best be appreciated by summarizing briefly the state of organic chemical theory at about 1860. In this light Butlerov's important contributions will be most easily evaluated.

After Berzelius' "Dualistic Theory," Dumas' "Type Theory," and Gerhardt's "Unitary Theory," Frankland in 1852 proposed the concept of atomicity or valence by postulating that a given element forms compounds by uniting with a definite number of what we now might call equivalents of other elements. Frankland was mainly concerned with inorganic chemistry, but in 1857 Kolbe extended this concept to carbon and said that carbon usually has a valence of four. Also in 1857 and independently of Kolbe, Kekulé deduced the tetravalence of carbon. In the May, 1858, issue of Liebig's *Annalen*, Kekulé (*36*) advanced the fruitful postulate that a carbon atom can unite with an indefinite number of other carbon atoms into open chains or (as stated a few years later) into closed chains or rings.

Gerhardt considered "rational formulas" to show nothing about the actual internal makeup of a molecule but merely ways in which compounds could react. Thus, he, Wurtz, and others wrote for a single compound different formulas for different reactions. Berzelius' followers considered a "rational formula" to indicate the manner in which a complex compound was composed of a union of groups of atoms (called radicals). Kolbe aimed at arriving at the chemical constitution of a compound in the special sense of showing the relationships between radicals within a molecule. He believed chemists were unable to determine the manner in which individual atoms were linked together. Some of his formulas, while descriptive, led to the prediction of more isomers than actually exist; for example, he wrote formulas I and II for acetone. Kekulé's formulas were rather bulky and difficult to handle, and he admittedly attached little physical significance to them. As an example, he wrote formula III for acetic acid.

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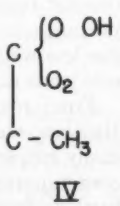


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Unaware of Kekulé's May, 1858, paper, Couper orally had presented his views on the tetravalence of carbon and the ability of carbon atoms to form chains. This occurred in a lecture to the newly formed Chemical Society of Paris on June 23, 1858; however, his paper (*37*) was not published until later that year.

Couper's formulas were easier to handle than those of Kekulé; thus, he wrote formula IV for acetic acid. Had he used 16, rather than 8, as the atomic weight of oxygen, this formula would be very close to modern ones. Couper had promised a second paper on this same general subject. However, he went insane,[7] and this paper never appeared.

## CONTRIBUTIONS OF BUTLEROV (1828–86) TO ORGANIC STRUCTURAL THEORY

We should now be ready to consider Butlerov's contributions in proper perspective. To be able to do so is of more than ordinary importance because in most of the Russian articles cited earlier in this paper Butlerov's contributions are repeatedly and ridiculously exaggerated in terms more chauvinistic and emotional than scientific. Above all, Butlerov is championed as the foremost exponent of the application of dialectical materialism to chemistry.

A few quotations will illustrate the prevailing Russian attitude:

> [Butlerov's] theory of chemical structure has been the dominant theory in organic chemistry for 90 years. Proving itself to be a truly scientific theory in the Marxist-Leninist sense of the term, and objectively disclosing the chemical relationships and phenomena existing within molecules, Butlerov's theory is characterized by great perceptional and regenerative power.
>
> Many of Butlerov's discoveries, which supported his predictions based upon the theory of chemical structure, met with no practical application in our country under Czarism. They made their appearance in production during the era of the remarkable Stalin Five-Year Plans of the U. S. S. R.'s national economy. This is a striking example of the bond between, the unity of, theory and practice (*14*).
>
> The Butlerov concept of hypermechanical chemical structure is a concretization of the Engels concept of hypermechanical chemical movement (*18*).
>
> Mendeleev's discovery of the periodic law and Butlerov's statement of the theory of chemical structure in chemistry are among the greatest historical events in natural science, outstanding successes of the materialistic Weltanschauung and victories of dialectical materialism over agnosticism and idealism (*14*).
>
> Soviet chemical theory must be freed from the influence of bourgeois theory and must develop within the plane of Butlerov's dialectical-materialistic teaching concerning chemical structure (*18*).

On September 19, 1861, Butlerov read a paper called "The chemical structure of compounds" to a scientific congress at Speyer, Germany. This paper contained the first use of the term "chemical structure." Butlerov considered it both possible and essential to express

[7] Recently Jacques (*38*) has presented interesting and scholarly evidence suggesting that Couper's insanity possibly may be traced to his extreme disappointment on seeing Kekulé's paper and his anger occasioned by Wurtz's delay in presenting his manuscript to the French Academy for publication. Jacques also suggests that Wurtz's delay was occasioned not entirely by his forgetfulness but partly by his low opinion of the paper. The excitable Couper impetuously questioned Wurtz about the delay, only to be promptly dismissed from Wurtz's laboratory.

the structure of a compound by means of a *single* "rational formula," which would show how every atom is linked to every other.

Although "Butlerov's paper was coldly received by the audience" (*16*), its presentation has been described as marking "the Rubicon that Butlerov crossed" (*16*).

That it should be possible to arrive at the correct structural formula by a study of different methods of synthesis of a given compound also was suggested by Butlerov. His belief that the single structural formula should designate the manner in which individual atoms of a compound are linked together was in marked contrast to Kekulé's opinion. Butlerov clearly stated that all properties of a compound should be governed by the actual, real manner in which each atom is linked to every other. It is perhaps no exaggeration to state that the main problem in theoretical organic chemistry since Butlerov's time has been and still is to relate the properties of organic compounds to their structural formulas.

Butlerov's assertion 93 years ago that each organic compound has a single, real structure very nicely fits into the materialistic ideas of present-day Communists. Butlerov is being highly praised for his materialistic doctrine, but Gerhardt and Kekulé are called agnostics. It of course seems certain that none of these early chemists was concerned with political doctrine when he propounded his chemical ideas.

There is no doubt whatsoever that Butlerov has not received the credit he richly deserves and that his monumental contributions to organic structural theory have been for the most part virtually overlooked. The Russian articles emphasize this point very strongly, and, despite its crude presentation, the point is well taken. Butlerov's contributions certainly equal those of Kekulé and Couper, but it is ridiculous to maintain that Butlerov is the *sole* author of structural theory. The ideological invective most of the Russian articles heap on the West while glorifying Butlerov is both irrelevant and nauseating.

The author, in his classes, now talks about the Kekulé-Couper-Butlerov theory of structure and endeavors to emphasize the separate, but complementary, contributions of each. That a German, a Scot, and a Russian are jointly responsible for such a great advance in chemistry illustrates how the erection of national barriers might hinder scientific progress.

The present paucity of information on Butlerov in the English-language chemical literature can only be deplored. Among the modern American textbooks on elementary organic chemistry the book by Cheronis (1941) appears to be the only one to even mention Butlerov's name until the appearance (in 1951) of Noller's excellent text. Cheronis accurately assesses (*39*) the separate contributions of Kekulé, Couper, and Butlerov, while Noller presents a brief biography (*40*) of Butlerov which emphasizes that he was the first to use the "concept of structure." The intense Russian resentment over the omission of Butlerov's name from American texts is illustrated by Danilov's scathing denunciation of Fieser and Fieser's text as "a distortion of the history of chemistry" which "indicates the lack of comprehension by these authors of the paths of development of organic chemistry" (*11*).

A few English-language books on history of chemistry give Butlerov brief mention. However, his name is not listed in the "Encyclopedia Britannica," whereas Kekulé receives a full column.[8] Between 1907 and 1952 apparently only one biography of Butlerov has appeared in the English-language chemical literature. This article (*41*), however, deserves special attention because it was written prior to the present state of extreme tension between East and West.

To show that lack of recognition of Butlerov has not been confined to America or the West it seems necessary to point out that even the great Mendeleev, who also has been highly praised in recent Russian literature, refused to use Butlerov's theory in his own lectures and continued to use a version of the substitution theory (*16*). Also, it is interesting to note that Butlerov's doctoral dissertation was presented in the spring of 1853 to the faculty of the University of Kazan, but this august body refused to accept it. On January 16, 1854, the dissertation was presented to the University of Moscow, where it was accepted, Butlerov finally receiving the doctor's degree on June 4, 1854 (*22*). Finally, to indicate that American recognition of Butlerov was not completely lacking, it must be mentioned that he was included in the selected group of chemists upon whom the newly formed American Chemical Society bestowed honorary membership in 1876. Butlerov accepted this honor most graciously (*41*).

A second great contribution made by Butlerov in his 1861 paper was his postulation that important relations exist between atoms not directly connected by valence bonds and that such relations are important in correlating chemical properties with chemical structure. This concept later was elaborated by Markovnikov (see below).

The third important theoretical idea of Butlerov's was presented in 1876, when he gave a clear definition of tautomerism for the first time. Here again, his contribution has been largely neglected. Laar, who introduced the *word* tautomerism in 1885, usually is given credit as the author of the *concept*. That Butlerov is not alone in having his contributions overlooked is demonstrated by the recollection that Victor Meyer usually receives credit for having introduced the important concept of steric hindrance in 1894 even though the less well known Kehrmann had used the term several years earlier.

From reading accounts of Butlerov in present-day Russian chemical literature, the uninformed could easily suspect that Butlerov had no association with his contemporary chemists. Actually, nothing could be further from the truth. In fact, Butlerov himself

[8] Interestingly enough, Couper also is not listed in the "Encyclopedia Britannica."

wrote that he changed "from a student to a scholar" (*41*) only after his first extended tour (June, 1857–August, 1858) of laboratories in Germany, France, and England. It should be noted that he again toured Western Europe in 1861, the year of his famous lecture at Speyer. His third trip lasted from August, 1867, to June, 1868 (*41*). It is well known that Butlerov and Kekulé were personal friends even before 1861. Undoubtedly they had a number of friendly conversations on chemical problems of the day, each fertile imagination stimulating the other. It seems certain that Butlerov valued, rather than spurned, his association with Kekulé.

Jacques (*38*) has discovered that Butlerov visited Wurtz's laboratory in Paris for several months during 1857, during which time Couper was also there. Both Butlerov and Couper at this time joined the newly formed Chemical Society of Paris. On February 17, 1858, Butlerov orally presented his views on the constitution of chemical compounds to this small group; four months later, Couper made the oral presentation mentioned earlier in this paper. Butlerov's lecture was supposed to have been published in *Comptes rendus*, but for some unknown reason it never appeared. In an impersonal and scholarly manner, Jacques (*38*) notes that there is no written evidence that Couper attended Butlerov's lecture. He concludes, however, that it would be difficult to believe that Couper was not at least aware of Butlerov's ideas and that Couper probably was stimulated by them to work on his own structural formulas. In turn, Butlerov probably was stimulated by Couper, as he was by Kekulé. Certainly it must be admitted that this "Big Three" of structural organic chemistry knew each other personally and profited thereby.

In the author's view, it is a sad commentary on modern Russia that the "Iron Curtain" would absolutely prohibit such association today. Russian chemical journals loudly proclaim the worthlessness of "capitalistic" science and state categorically that no real *scientific* progress can be made outside the framework of a *political* ideology called dialectical materialism. At present, many Russian scientific journals do not leave Russia and her satellites. The harm this situation is bringing to science both inside and outside Russia can hardly be overestimated. It may not merely be sarcastic to suggest that Russia, at present, is sowing the seed for additional foreign neglect of her scientific accomplishments in the future.

Any discussion of Butlerov's contributions to chemistry would be incomplete without reference to his most famous student, V. V. Markovnikov, known to all organic students for his famous "Rule."

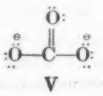
Although Butlerov's contributions to chemistry have largely been overlooked until recently, in general Russian contributions to chemistry have not been overlooked. To support this contention the names of other important Russian chemists are listed below in what is certainly a representative—but by no means exclusive—list. Almost every advanced student of organic chemistry in any country is familiar with the chemical contributions associated with each of these names: Arbuzov, Demjanov, Favorsky, Kishner, Markovnikov, Mendeleev, Nesmeyanov, Prileschaiev, Reformatsky, Tischenko, Tschitschibabin, Tschugaev, Zaitsev, Zelinsky, and Zerewitinoff.

## NATURE OF THE RESONANCE THEORY

In order to facilitate an evaluation of Russian criticisms of resonance theory it is imperative to summarize qualitatively the exact nature of this theory. For this purpose, let us now skip from Butlerov's day to about 1930 and examine some aspects of the state of structural theory in organic chemistry at that date. Prior to this time G. N. Lewis, and others, had suggested that a covalent bond be represented by a shared pair of electrons. This concept, together with the relative electronegativity of atoms and the developing knowledge of the total number of valence electrons normally possessed by the common atoms, permitted useful refinements of the older line formulas. However, it was becoming increasingly apparent that even the modernized Kekulé-Couper formulas precluded the accurate representation of many known properties of compounds, particularly aromatic compounds and open-chain compounds with conjugate unsaturation.

Above all, the modernized classical formulas permitted the expression of nothing but whole-number, that is, integral, bond multiplicity. Nevertheless, a lot of excellent experimental data appeared to necessitate unsaturation which, for example, was greater than that associated with a single bond but less than that associated with a double bond. Even the modern Russian chemical literature admits that this problem existed. (However, the Russians always hasten to add that Butlerov's concept of chemical structure does not necessitate only integral bond multiplicity. This statement is so obviously true that it is exceedingly trite; furthermore, it contributes nothing toward a solution of the problem of *formulation*.) Butlerov's statement that a chemical compound has only one real structure offers no means for writing that structure.

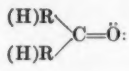
To turn to specific examples, it has long been known that all three carbon-oxygen bonds in the carbonate ion are of identical length, each being somewhat shorter than the standard carbon-oxygen bond distance in saturated compounds. That this fact cannot be reconciled with the classical formula (V) is immediately obvious. As another example, the measured dipole



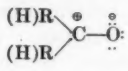
V

moments of a variety of aldehydes and ketones are virtually the same, much larger than can be explained by a completely covalent structure (like VI) and much

smaller than can be explained by a partly ionic structure (like VII).



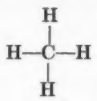
VI



VII

Obviously, one way of handling this distressing situation would be to discard the above type of structural formula, which has been used essentially since 1860. However, groups of chemists led by Fritz Arndt in Germany, C. K. Ingold in England, and Linus Pauling in the United States suggested ways and means of retaining these formulas but with an altered significance. Although the theories proposed by these three schools of thought had much in common, they received separate names, namely, theory of intermediate stages, theory of mesomerism, and theory of resonance, respectively. Pauling (*42*, p. 125) lists references to the original literature concerning the three theories. Very little inaccuracy will be introduced by referring hereafter to the theory of resonance as being representative of the new outlooks upon chemical structure.

Pauling emphasized that classical formulas (like VIII for methane) are quite satisfactory for many saturated compounds and have the advantage of being



VIII

understood by most chemists. Hence, *as a matter of convenience*, he suggested that classical formulas for such "troublesome" species as the carbonyl compounds also be retained but with the following significance.

The experimental data indicated that the true structure of the carbonyl group is intermediate between VI and VII. For this intermediate, real structure (called the hybrid) a conventional structural formula obviously cannot be written. However, this intermediate structure may be described as an appropriately weighted average of VI and VII; thus, VI and VII are designated "contributing structures" or electromers (since they differ only in the position of electrons).[9] Since the measured dipole moment is almost exactly halfway between the moments calculated for VI and VII, these two structures are considered to "contribute" equally to the resonance.

If, in addition to VI and VII, it were possible to write for a carbonyl compound other reasonable structures differing only in the position of electrons,[10] the contributions of these structures also would have to be assessed. The only practical limit to the number of "contributing structures" is chemical intuition based on well known rules of electron behavior. However, the very considerable arbitrary element thereby introduced is more than compensated for by the practical usefulness of the theory.[11]

Ingold's mesomerism theory has attempted to picture the true structure (hybrid) as

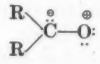
In fact, the term "mesomerism" (meso = between), which suggests that the hybrid has an intermediate structure, has an advantage over the term "resonance," which long has been used to describe an actual phenomenon in physics, because resonance in chemistry is not a physical phenomenon.

A second important concept used in resonance theory may be introduced by noting that measurable constants like the heat of combustion can be calculated with great accuracy for many chemical compounds. However, the experimental heat of combustion for a "resonating" compound always is *less* than the value calculated additively for any of the contributing structures. The difference between the observed heat of combustion and that calculated for the contributing structure of lowest energy is *defined* as the "resonance energy" of the compound in question. Resonance energies also may be determined from calculated and observed heats of formation, heats of hydrogenation, etc. This invented concept of resonance energy, though extremely arbitrary, is most useful.[12] Thus, we say a compound is "stabilized"[13] by an amount of energy equal to the resonance energy. Actually, resonance energy—the difference between the energy of the hybrid and that of the contributing structure of lowest energy—is an attempt to express quantitatively the extent to

[9] The author prefers not to use the word electromer, since it might be construed to imply a real existence for the species involved, whereas the resonance theory definitely states that these structures are no more than "intellectual constructions." Electromeric species have never been identified experimentally.

[10] Actually there are other requirements limiting the number of contributing structures, but these need not be considered for most purposes.

[11] That chemical intuition provides a reasonably satisfactory criterion of the number of structures considered is illustrated by the fact that no chemist would consider a structure such as

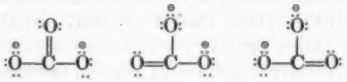


because the most electronegative atom does not bear the negative charge.

[12] That values determined as above should be called *experimental* resonance energies is somewhat unfortunate since the *actual* heat of combustion of a *hypothetical* contributing structure cannot be measured.

[13] This also is a poor word to the extent that it implies resonance to be a phenomenon of nature. However, while it is illuminating to realize that resonance is not a phenomenon of nature, the arbitrary aspects of resonance theory can easily be exaggerated. It is important to realize that one is as justified in saying a compound is stabilized by resonance as in saying that it is made unsaturated by a double bond. Even the carbon-to-carbon single bond is not a phenomenon of nature. In fact, one of the chief drawbacks to the acceptance of resonance theory has been the ingrained belief of many chemists that integral bond multiplicity is a fact of nature.

which classical formulas are poor representations of actual molecules. Resonance energy reaches a maximum when the contributing structures are identical,[14] as in the case of the carbonate ion:



A third important feature (which will not be discussed in detail here because of its mathematical nature) of resonance theory is Pauling's discovery that wave functions often can be assigned to hypothetical structures such as VI and VII. The wave function of the hybrid (real molecule) then can be expressed as a combination of the wave functions of the hypothetical structures.

## RUSSIAN CRITICISMS OF RESONANCE THEORY

The general flavor of these criticisms can be appreciated by noting the following phrases used in recent Russian chemical literature to describe the resonance theory: (1) "has a methodologically faulty basis," (2) "built on incorrect basic assumptions," (3) "an example of world outlooks hostile to the Marxist view," (4) "presents perverse philosophical outlooks," (5) "has lost contact with practice," (6) "inconsistent with generally known facts," (7) "philosophic setting is Machistic," (8) "does not reflect objective reality," (9) "leads to pseudoscientific conclusions," (10) "leads to absurd consequences," (11) "bankrupt and sterile," (12) "profoundly erroneous," (13) "scientifically insolvent," (14) "vicious," (15) "harmful," (16) "idealistic," (17) "methodologically defective, physically groundless, and sterile," (18) "completely denies the whole content of the doctrine of Butlerov," (19) leads "to the reactionary concept of the unknowability of the existence of an actual chemical structure of a molecule."

Furthermore, G. W. Wheland is described as "a loyal servant of the reactionary bourgeoisie" . . . a "blunderer in physics and propagandist of Machism" . . . a man who "misrepresents for class reasons the history of the development of theoretical organic chemistry."

When separated from invective like the above, the Russian criticisms are amazingly devoid of content, but they may be divided into three main categories, as follows:

First of all, the Russians most vigorously assert that contributing structures (like VI and VII) have no real existence but that "resonance theoreticians" think they do. If that were true, apparently it would prevent a proper belief in materialism.

It is nothing short of ludicrous that one of Marxism's most devoted scientists, J. B. S. Haldane, in 1939 highly praised Pauling's resonance theory as "a beautiful example of dialectical thinking, of the refusal to admit that two alternates (two contributing structures) which are put before you are necessarily quite exclusive" (*44*, p. 101).[15,16]

Secondly, the Russians state that resonance theory assigns several structures to one compound and hence is a reversion to Gerhardt's "agnostic" views and is an attempt to displace Butlerov's theory of chemical structure.

Thirdly, resonance is denounced as a theory of mere utility and convenience. The arbitrary nature of the choice of contributing structures is repulsive to the Russians because it contradicts Leninist-Marxist views. This criticism is entirely ideological, and it is stated in the most revolting terms.

Since the three categories of Russian criticisms are closely related and certainly not mutually exclusive, no rigorous attempt will be made to evaluate them separately.

The first two categories contain no substance whatsoever simply because resonance theory does *not* attribute real existence to "contributing structures" and does *not* assign several structures to the same molecule. Hence, these criticisms appear to be nothing more than vicious attempts to mislead the uninformed. Good definitions of resonance cannot be found in the Russian articles cited earlier. In one article (*6*) only one part of Pauling's discussion of the question of the reality of contributing structures is quoted. This quotation, taken out of context, seems to prove the validity of the Russian point of view. The part not quoted by the Russian authors actually appears in italics in Pauling's book: "A substance showing resonance between two or more valence-bond structures does not contain molecules with the configurations and properties usually associated with these structures" (*42*).

The part of Pauling's discussion to which the Russians object is ". . . if it were possible to carry out an experimental test of the electronic structure which would identify structure I or structure II" (the Kekulé structures for benzene), "each structure would be found for the molecule to the extent determined by the wave function. The difficulty for benzene and for other molecules showing electronic resonance is to devise an experimental test which could be carried out quickly enough and which would distinguish among the structures under discussion" (*42*). Thus, "if the usual chemical significance is attributed to the structures" (*42*), the structures have no reality. Obviously the Russians choose not to attach "the usual chemical significance" to the structures.

Almost as if he were anticipating the Russian objection, Pauling further states:

[14] Although this conclusion can be reached on empirical grounds, Gero (*43*) has presented an excellent common-sense justification of the concept.

[15] It must be pointed out that Haldane had an erroneous idea of the nature of resonance, apparently believing it to be a special case of tautomerism.

[16] I am indebted to Dr. Pauling for informing me of Haldane's commendation.

> The discussion . . . regarding the element of arbitrariness in the concept of resonance may be recalled . . . with reference to the nitrous oxide molecule and the other molecules . . . described . . . as resonating among several valence-bond structures. It is not necessary that the structures A and B be used as the basis of discussion of the nitrous oxide molecule. We might say instead that the molecule cannot be satisfactorily represented by any single valence-bond structure, and abandon the effort to correlate its structure and properties with those of other molecules. By using valence-bond structures as the basis for discussion, however, with the aid of the concept of resonance, we are able to account for the properties of the molecule in terms of those of other molecules in a straightforward and simple way. It is for this practical reason that we find it convenient to speak of the resonance of molecules among several electronic structures.
>
> It is to be emphasized that in writing two valence-bond structures for the nitrous oxide molecule and saying that it resonates between them we are making an effort to extend the valence-bond picture to molecules to which it is not strictly applicable, and that we are not required to do this but choose to do it in the hope of obtaining a satisfactory description of these unusual molecules, permitting us to correlate and "understand" the results of experiments on their chemical and physical properties and to make predictions in the same way as for molecules to which a single valence-bond structure can be assigned. Nitrous oxide does not consist of a mixture of tautomeric molecules, some with one and some with the other of the two structures . . .; instead, all of the molecules have the same electronic structure, this being of such a nature that it cannot be satisfactorily represented by any one valence-bond diagram but can be reasonably well represented by two. The properties of the molecule are essentially those expected for an average of the two valence-bond structures, except for the stabilizing effect of the resonance energy (*42*, pp. 127–8).

It appears reasonable to accuse the Russian authors of either malicious intent or ideological slavery rather than stupidity. Of course, the extent to which qualified Russian chemists are ideological slaves of the Kremlin is not known to the present author. However, it is very probable that some qualified chemists are forced to subjugate scientific thinking to ideological necessity. Since scientific journals traditionally have operated on the unstated, but unquestioned, assumption of the intellectual integrity and freedom of the individual scientist, this subjugation possesses the potential for extremely grave damage to Russian theoretical science.

The Russian assertion that each molecule has only one structure very likely is correct, but what today is designated as a single chemical species could tomorrow (because of refined experimental methods) be composed of several different species. Thus, caution should be applied in this regard to a substance *presently* believed to be a single species.[17] Of course, resonance theory does not assign several structures to one chemical species. The one species is the hybrid, for which a single classical representation is impossible. It would therefore seem extremely difficult to conclude, as the Russians do, that resonance theory contradicts Butlerov's doctrine that each compound has only one real structure.

One of the important values of resonance theory is its usefulness in connection with visualizing activated states of molecules. Although contributing structures (like VI and VII) do not exist in the normal resting state, addition reactions of carbonyl compounds are nicely explained by assuming that during chemical reaction the hybrid transiently forms the energized species VII and that VII is the species actually undergoing reaction. Now this in no way invalidates any belief that under ordinary conditions a compound has only one structure. However, *during* chemical reaction a resonating compound may behave as if it has any one of the contributing structures (such as VII). Hence, the contributing structures roughly correspond to activated states. This concept would appear to be the modern explanation of the old problem which long ago gave rise to the different "reaction formulas" of Wurtz, Gerhardt, and others. Incidentally, the Russians appear to take no notice of this aspect of resonance theory.

[17] The discovery of isotopes should be recalled at this point.

## DIFFERENCES IN RUSSIAN ARTICLES ON RESONANCE BETWEEN 1949 AND 1952

To say that a definite pattern of change has emerged in the stated period certainly would not be justified. However, between 1949 and 1952 some articles have tapered off in invective against resonance. In fact, occasional statements are found which might be construed as disguised support for the notion that at least some parts of resonance theory may not be criminal. Other articles appear to contain *both* veiled praise and intense dislike for the resonance theory at different places in the same discussion.

One article by A. E. Arbuzov (*16*), published in 1952, contains absolutely no invective. This long article on Butlerov says virtually nothing about resonance theory and presents an evaluation of Butlerov's contributions to chemistry that appears to be quite fair. More than half of this paper is devoted to the important contributions to chemical theory made by well known English, French, and German chemists. In this light Butlerov's contributions then are evaluated. In an attempt at fairness, I have based my earlier discussion of pre-Butlerovian chemical theory largely on Arbuzov's paper.

That this trend does not denote a complete change of attitude is indicated by the fact that late in 1952 Syrkin and Dyatkina (*21*) (the previous champions of resonance in Russia) finally admitted their "errors," denounced the resonance theory, and promised to mend their ways. It is significant that these very talented chemists state that "over forty years ago V. I. Lenin, in his work of genius 'Materialism and Empiriocriticism' liberated the natural sciences from mysticism and Machism. . ." (*21*). They continue with: "Comrade Stalin's work 'Marxism and the Problems of Linguistics' teaches all those who are active in Soviet culture how to apply veritable partisanship to science, this partisanship being diametrically opposed to bourgeois objectivism. At the same time, veritable partisanship in no way rejects a really objective analysis of natural phenomena, inasmuch as really scientific, objective explanations of the laws governing the world

of reality are always and in every case found to confirm the correctness of dialectical materialism" (*21*). Fanatics in every age have been guilty of such "veritable partisanship" without ever having been able to justify it.

Syrkin and Dyatkina readily admit the "erroneous nature of those of our papers in which we made use of this [resonance] theory, or supported it" (*21*). In great detail they confess grave errors in their book "The Chemical Bond and the Structure of Molecules." They solemnly promise: "We shall in our future work make every effort toward the rectification of our mistakes. Our future task will be to contribute to the development of knowledge of the structure of molecules on the lines of the teachings of dialectical materialism and of the ideas of Butlerov, Mendeleev, Markovnikov, and other coryphaei of Russian science" (*21*).

An exception to the trend toward less invective is found in the work of Chelintsev, who in 1952 published two papers (*15*, *18*) crammed with unreasonable ideological tirades. These papers contain the least scientific statements I have ever seen in any presumably scientific literature. For example, Chelintsev fumes: "The notation comprised in the Ingold and Pauling formulas has resulted in a quandary pregnant with evil consequences" (*15*). Chelintsev's remarks are so crude that several Russian authors are provoked to state vigorously that, while resonance theory cannot be tolerated, Chelintsev's criticisms are way off base. There thus appears to be some rivalry within the ranks of Russian chemists as to just how much unreasoned abuse is permitted.

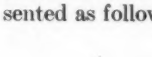
Apparently Chelintsev was the first to insist that resonance theory does not agree with the dialectical materialism of Lenin, Marx, and Stalin. He seems to believe that this in itself lends great weight to any of his arguments.

Illustrative of Chelintsev's incomprehensible attitude is his paper (*15*) which criticizes the editorial articles by Kazansky and Bykov which appeared in the recently published (in Russian) volume of Butlerov's collected works. Kazansky and Bykov are accused of maintaining that Butlerov's ideas on chemical structure were "a lucky mistake that proved to be fertile from the practical standpoint" (*15*). Although it seems doubtful that any present-day Russian would dare to make such a statement about Butlerov, the answer to this riddle very likely is contained in Kazansky and Bykov's article (*31*), which unfortunately I have been unable to obtain in translation. It is possible that Chelintsev had desired to have the honor of writing the aforementioned introduction himself.

Chelintsev also has the audacity to accuse the Commission of the Division of Chemical Sciences of having issued a report which did not denounce the resonance theory forcefully enough! (*15*). Possibly this may be attributed to the severe criticism of Chelintsev's "New Structural Theory," which also was contained in the Commission's Report.

That additional disagreement exists within Russian chemical ranks is illustrated by Reutov's parenthetical remark that the great Butlerov had endorsed the criterion of convenience in these words: ". . . 'any method of notation may be good, provided it expresses these [chemical] relationships conveniently' " (*12*). Earlier Sokolov (*7*) had noted the same quotation from Butlerov. Quickly thereafter, Danilov comes to the rescue by insisting that Butlerov never advocated using anything merely for convenience, but it is worth while to note that the word "conveniently" is replaced in Danilov's article by "satisfactorily" (*14*).

Part of one of Reutov's articles appears to point out that resonance theory is not entirely vile. Thus, he admits that neither of the contributing structures can explain the measured dipole moments of aldehydes but that the correct structural formula "is usually represented as follows:



Thus, representing a molecule by means of several formulas . . . is frequently a step on the road to the establishment of a single rational formula" and "this road is justified both logically and, in many cases, historically" (*12*). An attempt to reconcile this statement with one made earlier in the *same* article appears hopeless: "Establishing the *semblance* of an explanation of an extensive group of phenomena in organic chemistry, the 'theory of resonance' distracts the attention of chemists from the solution of essential scientific problems, diverting their efforts to the fallacious path of seeking the causes of the chemical structure of molecules and their reactivity in the property of fictitious 'resonance structures' and in the nature of the nonexistent phenomenon of resonance. Because of all this, the 'theory of resonance' is a brake upon the further development of the theory of organic chemistry and must be excluded from the arsenal of chemists" (*12*).

As early as 1949 Sokolov made statements that actually constitute moderate praise for the resonance theory: ". . . the development of this method" (Pauling's resonance symbolism) "was an advance over the classical theory of valency since it provided the possibility of fuller consideration of the mutual influence of atoms in molecules. . . . When it is desired to represent a molecule by an array of 'structures,' consideration is given as a rule not only to the formal laws of valency but in the main to a specific combination of known experimental facts (properties of symmetry, chemical analogs, dipole moments, bond lengths, etc.). There is nothing objectionable in such a representation. . . . This mode of notation may later play a constructive part in chemistry, although it will not then be Pauling's 'Theory of Resonance' " (*7*).

## CHELINTSEV'S "NEW STRUCTURAL THEORY"

In this section will be discussed what apparently is the lone Russian attempt to replace the resonance theory with another theory. Frequent quotations

from Chelintsev's articles will be used to illustrate the utter worthlessness of his theory.

In 1949 G. V. Chelintsev, perhaps the first, most severe, and most unrestrained critic of resonance, published a book entitled "Notes on the Theory of Organic Chemistry," in which his "New Structural Theory" was presented. [18] This theory was briefly explained (and vigorously criticized) in a Russian article which appeared in English translation in 1952 (*6*).

Chelintsev's theory may be illustrated by reference to his formula (IX) for benzene. He describes this formula as "the only possible, and practically complete, formula for benzene on the basis of contemporary

IX

electronic and nuclear concepts" and then offers the following rather inclusive claim: "This formula combines all the experimental data on the properties and the mechanical state of benzene, of its analogs, its homologs, and its derivatives" (*15*).

Despite the above claims, Chelintsev is forced to admit that three obstacles have hindered adoption of his theory. To overcome the first one, which he claims to be "of a superficial nature," Chelintsev declares that "the plus and minus signs in the cited formula represent the atomic charges rather than the electron distribution" (*15*). He says that the six electrovalent bonds indicated above are more stable than the three covalent bonds used in the Kekulé formula. However, Chelintsev's formula would appear to contain six ionic bonds, each of which is one-half of a "full" electrovalent bond, since each charged atom is forming a bond with two oppositely charged atoms. The six "extra" electrons of benzene certainly cannot be responsible for six "full" electrovalent bonds within the molecule. Chelintsev himself admits that three covalent bonds are more stable than three electrovalent bonds. That Chelintsev's preposterous formula for benzene should be published by any reputable scientific press seems very difficult to understand.

To the second objection, which he regards as "more serious," Chelintsev gives this fantastic reply:

> We have to overcome the customary notion of the electrovalent bond as that of a polar bond. We have to convince chemists of the feasibility of a homopolar electrovalent bond. Notwithstanding the apparent paradoxicality of the concept of a homopolar electrovalent bond, it has a logical foundation . . . we cannot reject the assertion that in the formation of an electrovalent bond between two equally electrophilic atoms (say, between two carbon atoms), the electron density ought to be distributed uniformly. . . . There remains the problem of what may serve as the cause of the formation of an electrovalent bond between equally electrophilic atoms, rather than a covalent bond. . . . The six electrovalent bonds doubtless represent an increase in energy over three covalent bonds. The reason for the formation of an electrovalent bond between equally electrophilic atoms may be the increase in energy that accompanies the conversion of one covalent bond into two electrovalent bonds. Thus, the concept of a homopolar electrovalent bond is not logical nonsense. The reality of this concept is given by the fact that it is the only one that opens up the possibility of providing a practically and methodologically complete solution of the problem of the structure of conjugated compounds (*15*).

Apparently not satisfied with the preceding, Chelintsev, at another place, says: "Let us see, however, whether the concept of the homopolar electrovalent bond is quite as absurd as it appears at first glance" (*18*). Then he continues to explain a "leveling-out" of the polarity when the two atoms are equally electrophilic. Perhaps the broken lines in his benzene formula are intended to indicate this "leveling-out."

The third objection to the adoption of his benzene formula is, according to Chelintsev,

> . . . of an ideological nature. The justification for . . . a homopolar electrovalent bond is founded upon the notion of the supramechanical phenomenon involved in the attachment of electrons to nuclei. This concept is in conformity with the Butlerov concept of chemical structure—the qualitative difference between the relationships of linked and unlinked atoms being due to the qualitative difference in the relationships between the electrons and the nuclei. From the mechanical standpoint, however, the attachment of electrons to nuclei is a matter of the distribution of electron density about the nuclei, so that the notion that, in addition to the general space-force relationships between electrons and nuclei within molecules, there exist some other, peculiarly combining-chemical relationships does not enter the mind of the "contemporary chemists" (*15*).

Chelintsev concludes his discussion of these objections to his benzene formula by noting:

> This formula deserves to live, since it alone provides a way out of the practical and methodological blind alley into which chemical theory has been led by the "contemporary chemists." The solution of the problem of the structure of conjugated compounds provided by this formula is another splendid triumph of A. M. Butlerov's theory of chemical structure (*15*).

Critics of Chelintsev's theory have not been slow to appear inside Russia. Outside Russia virtually no criticisms have appeared, probably because the theory is so patently useless and wrong.

Critics within Russia have included Reutov, Kazansky, Bykov, Sokolov, Kursanov, and most notably A. N. Nesmeyanov, president of the Academy of Sciences and an accomplished chemist. These authors heap ridicule on Chelintsev by fairly logical processes, but Nesmeyanov's criticism is the most devastating.

Before Nesmeyanov's criticisms are reviewed, it may be instructive to obtain a further grasp of Chelintsev's unique method of argumentation:

> . . . Nesmeyanov writes: "Why does Chelintsev never make use of this New Structural Theory for scientific purposes (and only for the purpose of unrestrained self-praise). . . . Why on the basis of the New Structural Theory has its author not made an attempt to make even a very limited prediction of new facts, not to speak of the verification of such predictions by experiment? It seems to me that there is only one answer. The author of the theory is convinced of its worthlessness—and so am I."
>
> The question of why I do not use the New Structural Theory for scientific purposes is an obscure one. Is not my use of this theory for solving the question of the structures of hundreds of

[18] Chelintsev's book was not available to the author.

thousands of conjugated compounds, for confirming the truth of Butlerov's dialectical-materialistic teaching concerning chemical structure, for refuting the sterile Machist mesomerism-resonance theory, and for the elimination of servility and Machism from Soviet chemical science—is not my use of this theory for these purposes indeed an application of the theory for scientific purposes? As far as my conviction of the worthlessness of the New Structural Theory is concerned, is it really possible to suppose that for a number of years I could bear the whole weight of the struggle with the Ingold-Paulingites that were monopolizing Soviet chemical science, if I were not deeply convinced of the correctness and usefulness of my ideas?

There remains the question of the possibilities of prediction in the New Structural Theory. It is a great pity that this question was not put at the correct time with respect to the theory of resonance. It was several years before Nesmeyanov admitted that "The explanations given by resonance theory are illusory and, at the best, consist only of descriptions by means of an assembly of formulas." Evidently, for the determination of the possibilities of prediction in a theory, time and practice are required (*18*).

Chelintsev's theory postulates two types of bonds, orbit and contact. Orbit bonds appear to be exactly the same as covalent bonds and, in the words of Nesmeyanov, "differ from covalent bonds only in name" (*19*).

Contact bonds, or homopolar electrovalent bonds, are ridiculed by Nesmeyanov in the following terms:

> So long as a contact bond is understood as an ionic bond, just as a covalent bond is equivalent to an orbit bond—all is in order. When in a molecule of ionic structure $A^{\bullet}B^{\circ}$ we assume the polarization of the electron cloud of the anion by the cation, we again are concerned with methods of looking on these matters that are understood and have been applied for a long time in science.
>
> If the atoms A and B are identical, then we may assume an unstable state $A^{\bullet}A^{\circ}$. However, if we imagine polarization of the anion $A^{\circ}$ by the cation $A^{\bullet}$ in such a way that the electron density will be distributed symmetrically about both A atoms . . ., then the molecule would be homopolar, non-dipolar, but at the same time the electrons of the shell of the former anion $A^{\circ}$ would continue to belong to it and only to it, which means abandoning science and assuming purely juridical relations between the two A atoms. This is what is meant by a homopolar contact bond. Withdrawal from the axis of third-order symmetry [see below] and acknowledgment of an axis of sixth-order symmetry in benzene is significant in that it is an acknowledgment that these juridical relations leave no material trace in the molecule.
>
> Is this really materialism? Is this not a manifestation of free will, if not of the electron, then of the nucleus? Have these "connective relationships" of electron and nucleus really got very far away from the life force? If it were not for these juridical relations, then with such a complete leveling-out of electron density, $A^{\bullet}A^{\circ}$ would change into A-A with a covalent, or as Chelintsev wants to call it, orbit bond. Thus, the ability of a contact (*i. e.*, electrovalent) bond to be homopolar, which is essential for Chelintsev's theory, is illusory and can in no way be justified . . . (*19*).

Nesmeyanov, and others, have pointed out, in addition to the above, two other serious errors in Chelintsev's theory. First of all, Chelintsev originally asserted that the coplanarity of olefin and aromatic molecules can be derived from the properties of the contact bond as being a bond of octahedral origin. Secondly, Chelintsev attributed to benzene an incorrect axis of third-order symmetry. To make matters worse, he used symmetry characteristics of *benzene crystals* as if they were identical with symmetry characteristics of *benzene molecules*.

In one short paragraph Chelintsev admitted these two errors and then crisply added: "Nevertheless, these errors, like many others which may be found, in no way affect the basic principles of the New Structural Theory" (*18*). However, Nesmeyanov explains in great detail that, without these wrong assumptions, Chelintsev has no theory left.

Perhaps the choicest observation Nesmeyanov makes is that Chelintsev equates all critics of his theory, present and future, with Ingold-Paulingites. Nesmeyanov's article eloquently concludes with: "Our chemistry must be thoroughly cleared of all the unhealthy influences of corrupt bourgeois philosophy and science. It must be cleared also of vulgarization of home origin" (*19*).

That the previously cited Committee Report (which rejected resonance theory) not only did not authorize, but vigorously denounced, Chelintsev's theory can only be commended.

## CONCLUSION

The effect to be expected from intrusion of Stalinist ideology into Soviet science has been analyzed from the rather short-range military standpoint in numerous articles in the popular press. However, the possible effects of this intrusion on the long-range development of theoretical science in Russia have not been widely discussed.

At present we might well recall the severe criticism of research in the early days of Communism in Russia, which was stated by the Marxist Haldane: "In the first 10 years of scientific research in the U. S. S. R. certain writers—one can hardly dignify them by the title of workers—attempted to apply dialectical materialism to every kind of activity from portrait painting to fishing. They produced a great deal of utter nonsense. Indeed the worse a scientific paper was, the more likely it was to be embellished in the irrelevant quotations from Marx, Engels, and Lenin" (*44*).

It seems no exaggeration to predict that very few fundamental advances in theory can occur as long as Soviet scientific thinking must follow the caprices of dialectical materialism and the "veritable partisanship" it requires.

## ACKNOWLEDGMENT

I am indebted to Dr. Linus Pauling for his valuable criticism of this paper. In particular, the contents of footnote 13 were suggested by Dr. Pauling.

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# A CELL FOR THE PREPARATION OF SMALL QUANTITIES OF ALKALI METALS[1]

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OWING to the high costs and small yields of the methods currently available for isotopic separation (*1*), the conversion of isotopes as compounds to the metals will necessarily be confined to a small scale. The work described here deals with the development of a miniature cell designed for the preparation of alkali metals from small amounts of their salts. The experiments were carried out primarily with lithium salts, although metallic potassium was also prepared in the same type of cell.

## CHOICE OF METHOD

Lithium was chosen for the developmental work because it is one of the least reactive of the alkali metals and was expected to be safe. Also, of the three alkali elements that have more than single naturally occurring nuclides (lithium, potassium, and rubidium), the $Li^6$ isotope is more abundant than the 40 and 41 isotopes of potassium, and lithium is more important industrially than rubidium, so that the lithium isotopes might be expected to be separated first. It was hoped, in any case, that the method finally worked out for lithium would, without major changes, be suitable for the preparation of the other alkali metals.

From the standpoint of the efficient use of any isotopic salts which might become available, the essence of the problem seemed to lie in determining how small an apparatus could be made that would still permit preparation of suitable quantities of metal. It was felt that one-half to one gram of recovered metal should be enough to allow most desired measurements. Several methods were considered:

(1) *Electrolysis of Solutions of Salts in Nonaqueous Solvents such as Ethylene Diamine, Pyridine, or Liquid Ammonia* (*2, 3, 4*). From the standpoint of hold-up, it was thought that solutions of salts certainly would be advisable, since the concentrations of the solutions could be quite low and the volumes small. Some work was carried out electrolyzing solutions of lithium salts in pyridine, but in spite of reports to the contrary, considerable difficulty was experienced in obtaining deposits of appreciable thickness that remained shiny. There appeared to be a reaction of the metal with the pyridine. Furthermore, the problem of collecting a thin deposit of the metal from the electrode was difficult. It was anticipated that ethylene diamine would be quite similar to pyridine, but because of the hazardous nature of the material, it was not tried. Articles dealing with the use of liquid ammonia as a solvent from which to deposit alkali metals were promising, but the apparent difficulty in setting up a liquid-ammonia electrolysis system led us to consider other possible methods first.

(2) *Chemical Reduction* (*5, 6*). Chemical methods were investigated and some reactions were carried out using the oxide, fluoride, carbonate, hydroxide, and halides of lithium, with magnesium, calcium, carbon, iron, barium, and ferrosilicon as reducing agents. The results showed varying degrees of success but the limiting size of reactor was larger than seemed desirable; it also seemed very probable that these methods could not be applied to those alkali metals more active than lithium.

| *Salt*[a] | *Sp. gr.* | *M. p., °C.* | *g. salt per g. metal* | *cc. salt per g. metal* |
|---|---|---|---|---|
| LiCl | 2.07 | 614 | 6.1 | 3.0 |
| LiBr | 3.64 | 547 | 12.5 | 3.4 |
| LiI | 4.06 | 446 | 19.3 | 4.8 |
| KCl | 1.99 | 790 | 1.9 | 1 |
| KBr | 2.75 | 730 | 3.0 | 1.1 |
| KI | 3.13 | 723 | 4.2 | 1.4 |
| RbCl | 2.76 | 715 | 1.4 | 0.5 |
| RbBr | 3.35 | 682 | 1.9 | 0.6 |
| RbI | 3.55 | 642 | 2.5 | 0.7 |

Data from Lange's "Handbook of Chemistry," 8th ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952.
[a] Oxygen-containing compounds were not even considered for fused-salt electrolysis on account of the interfering side reactions which occur.

(3) *Electrolysis from Aqueous Solutions with a Mercury Cathode* (*7*). A few experiments were carried out using a rather concentrated solution of lithium bromide in water with a sintered-glass barrier and a mercury cathode. Although deposition appeared satisfactory in small amounts, it has been reported that the solubility of lithium in mercury is small (*8*) and that the separation from an amalgam is difficult, owing to the great stability of some of the intermetallic compounds formed (*9*). Admittedly, these arguments might not hold for the other alkali metals.

(4) *Electrolysis of Fused Salts* (*10, 11*). The re-

[1] This article is based on work performed for the AEC by Carbide and Carbon Chemicals Co., a division of Union Carbide and Carbon Corp.
[2] As a Research Participant from Bradley University, Peoria, Illinois.

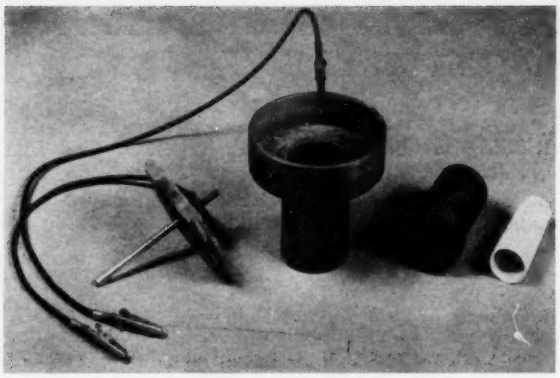

Figure 1. Electrolytic Cell

sults of preliminary trials with fused salts showed enough promise of success that the work on the other methods was, for the time being at least, abandoned and efforts were directed toward the fused-salt method.

## DEVELOPMENT OF THE CELL

In constructing a cell for the electrolysis of small amounts of salts, there were a number of factors to be considered:

(1) As seen from the table, the volume of salt per gram of metal is rather small in all cases. It is most advantageous in the case of lithium, particularly with LiI. But since deposition of iodine seemed less desirable than formation of chlorine at the anode, the iodide was not used. And since there was no great advantage in using bromide rather than chloride, the latter was used in all cases. The use of other salts as additives to increase the volume, with the possible necessity of a distillation for purification, was ruled out as unsuitable for small quantities of metal where recovery of the distilled material might be difficult (*12*).

Figure 2. Smaller Electrolytic Cell

(2) In any batchwise electrolytic process, hold-up in the cell is considerable. Most commercial cells operate continuously so that this factor is relatively unimportant (*11*), but where the raw material is to be limited, hold-up should be kept to a minimum.

(3) The materials of construction should be such that they will retain the molten salt, yet not react appreciably with it or with the products of the electrolysis.

(4) The minimum size of the cell would be limited by the fact that separate anode and cathode compartments are essential to prevent interaction of the products of electrolysis. Furthermore, the barriers in the usual industrial cells might no longer function efficiently in that capacity in very small cells where anode and cathode are in close proximity.

(5) The actual dimensions would be determined also, to some extent, by the materials of construction that are available.

## CELL PARTS

Of all the parts of the cell, the diaphragm seemed most critical. Stainless steel sheet and gauze and Inconel sheet and gauze were attacked by the chlorine evolved during the electrolysis; calcium fluoride, porcelain, alumina, thoria, zirconia, beryllia, and magnesia were attacked to various degrees, either by the molten salt or by the metal formed during the reduction. Alundum was finally chosen, primarily because small thimbles were readily available in various sizes, whereas the magnesia and beryllia, which were slightly more resistant, would have required special fabrication.

For the cathode, stainless steel seemed to work best. The cathode diameter did not seem critical as long as the current was not too high.

For the anode, carbon or graphite was almost mandatory to prevent reaction with the chlorine. The decision to make the anode also the container was one of expediency, since it permitted a smaller cell than otherwise would have been possible. It did have the disadvantage, however, of absorbing a small amount of salt as the electrolysis proceeded.

To permit heating of the cell and to retain any salt which might soak through the anode, the graphite was inserted in a stainless steel container which, in turn, was wrapped with a Calrod heater.

The connection from the power source to the anode actually was made through a clip lead fastened to a small piece of rod welded to the edge of the steel container. It had been found that connections directly to the graphite were short-lived, owing both to the corrosion of the clip lead by the escaping chlorine and to the oxidation and spalling of the graphite as a result of contact with the air.

## FINAL CELL

The size of the final cell, representing what seemed to be the optimum conditions with respect to a number of factors, was governed by the experiences encountered in resolving the difficulties that arose during the investigation. When the cell dimensions were too small, the lithium metal came in contact with the alundum very shortly after electrolysis had begun, and remained there until removed, reacting slowly with the alundum throughout the entire period. Also, when the cell was small, the escaping chlorine formed bubbles in the molten salt and carried the salt up between the graphite and alundum, depositing it as a solid around the top of the cell. The most serious difficulty, however, was what seemed to be the tendency of the chlorine gas to diffuse through the pores of the alundum, then to react with the metallic lithium in the

cathode compartment. By enlarging the cell slightly, these difficulties were either alleviated or eliminated entirely.

The final cell is shown in Figure 1, and a smaller version (but with the same cross-sectional dimensions) in Figure 2. The materials of construction comprised a $^3/_{16}$-in. stainless-steel cathode supported in a soapstone "yoke,"[3] a $1^1/_2 \times 3$-in. graphite crucible with 0.080-in. wall serving as combined anode and anode compartment, and a $1 \times 2^7/_8$-in. alundum thimble[4] as a diaphragm and acting also as the cathode compartment.

## CELL OPERATION

After the salt had been introduced into the cell and the temperature raised to the melting point, the cathode was inserted and current turned on. In a few seconds the cathode became coated with a shiny deposit of metallic lithium. As electrolysis continued, the deposit of lithium increased in size and soon was in the form of a large drop or pool surrounding the cathode. When the cathode was removed, the drop could be observed floating on top of the fused salt. The drop remained as a perfectly shiny globule, although apparently exposed to the air. The explanation seems to lie in the presence of a thin layer of molten salt over the surface of the metal (*13*), and the combination of this with the protection afforded by the slow escape of lithium chloride vapor was sufficient to prevent oxidation.

If electrolysis was carried out over an extended period of time a small amount of lithium chloride eventually seeped through the graphite container. This allowed some electrolysis at the surface of the stainless steel container and the consequent attack on the metal by the chlorine.

With the particular type of cell described, the usual charge was 35–40 grams of reagent-grade lithium chloride, though as little as 20 grams and as much as 55 grams could be charged. It was found that the time of operation could be extended and the total amount of recovered metal increased by adding more salt to the cell as the salt level was lowered. The yield immediately available as metal was in the order of 40 per cent based on the salt charged. Continued operation (at decreased efficiency) increased this somewhat. By extracting the contents of the cell with water and dilute HCl and then treating with appropriate reagents, it was possible to recover the remaining LiCl. Total recovery, including metal and salt, was 95 per cent of the original charge.

## REMOVAL OF LITHIUM FROM THE CELL

Removal of the lithium metal was carried out by use of a stainless steel pipet, coated on the inside with a thin layer of oil (Figure 3). A technique was developed in which the molten metal was drawn into the pipet until salt started to enter the tip. At this time the salt solidified, thereby plugging the pipet tip and retaining the lithium metal. It was now possible to extrude the metal quite readily by means of a plunger. The metal could then be coated with oil or simply allowed to nitridize in air to form a protective coating of its own. The former method was found to be the more satisfactory.

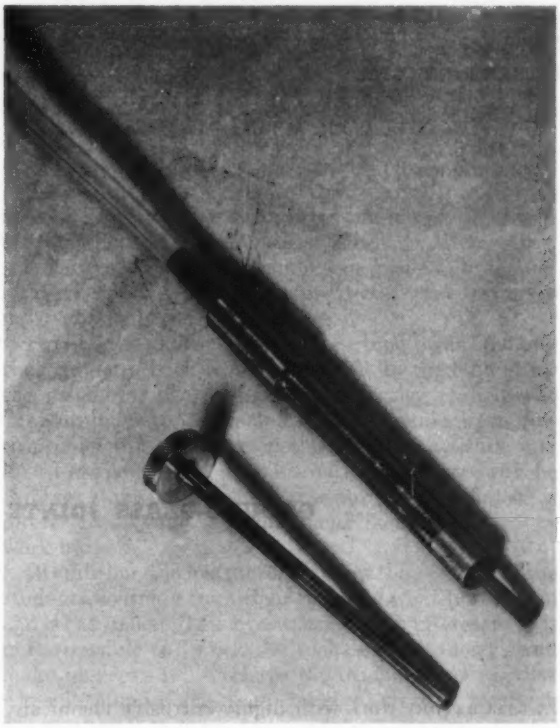

Figure 3. Pipet and Extruder for Lithium Metal

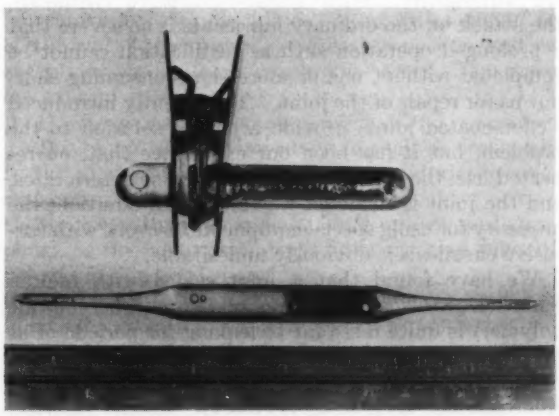

Figure 4. Metal Samples Under Oil, in Glass

[3] The decision to insert the cathode at the top was reached after many unsuccessful attempts to introduce it through the bottom by use of a Kovar seal. (The molten salt gradually worked into the seal, and electrolysis took place there.)

[4] Norton RA 360, No. 5163.

On numerous occasions, several of these extruded pieces were melted together in mineral oil, then pipetted into glass tubing to give pieces weighing several grams. In some cases the glass tubes were sealed off and in others the pieces of metal were removed into containers filled with oil (Figure 4). Both types of containers have kept the lithium shiny for over two years.

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## GROUND-GLASS JOINTS LEAKPROOF TO CORROSIVE CHEMICALS


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IN LABORATORY work with highly corrosive chemicals, the use of glassware with ground joints is often complicated by attack of the chemicals on lubricants required to obtain a good joint seal. This attack usually results in leaks through the joint during an operation and in severe sticking of the joint. The loss of material through leaking from a process is undesirable in any case, but particularly so where corrosive chemicals are concerned, because of the resulting contamination of the atmosphere. With certain corrosive chemicals, the attack on the ordinary lubricants is so severe that a prolonged operation such as rectification cannot be completed without one or more time-consuming shutdowns for repair of the joint. The recently introduced Teflon-coated joints provide a partial solution to the problem, but it has been our experience that, on repeated use, the coating tears or otherwise deteriorates, and the joint is rendered worthless. In addition, the necessity for using special equipment for work with corrosive chemicals is obviously undesirable.

We have found that a joint sealed with molten Saran (Dow Chemical Company's vinylidene chloride polymer) is quite resistant to leaking for periods of as much as 240 hours or more when used with certain corrosive chemicals at reflux. These chemicals include chlorosulfonic acid, sulfuryl chloride, thionyl chloride, fuming nitric acid, phosphorus oxychloride, phosphorus trichloride, phosphorus tribromide, and various organophosphorus halides. Effectiveness of the seal with other untested materials is probable.

The seal is prepared as follows. Small pieces of Saran tubing are partially melted on a metal spatula and placed on the clean male joint. The joint is heated in a flame, and the molten plastic is evenly spread over the surface with the spatula. It is then rapidly inserted into the female joint, and, while the plastic is solidifying, it is turned several times with pressure to obtain a uniformly coated, tight-fitting seal. To open the sealed joint, it is warmed with a flame and separated when the plastic has softened. The joint is cleaned by thorough wiping while the plastic is molten. Scrubbing with a detergent and hot water will destroy and remove any adhering film.

This sealing procedure has been used with standard taper as well as ball and socket joints. The seal is effective when used in an operation at a temperature above the softening point (about 120°C.) of the plastic. We have used the seal for work at both atmospheric and subatmospheric pressures. This type of seal is quite versatile in that it can be applied as needed to practically any piece of ordinary ground-glass equipment. Although Saran is the only commercial plastic we have used, it is possible that other chemically resistant thermoplastic polymers may be similarly useful.

# LABORATORY TEACHING

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Not all the bromides in the chemistry laboratory are in bottles. Some stand up in front on two legs, pompous, wordy, bored, looking down at helpless, equally bored freshmen, who are away from home for the first time, and quite bewildered. These teachers would be surprised if they could see what was in the freshmen's minds.

At the outset it must be recognized that few of the latter are there of their own volition. Chemistry is an entirely new language for the majority of freshmen, and they are not interested in it as such. They have all heard that it is a hard course, and would like to have avoided it. But all of them have some idealistic vision of themselves as doctor, dentist, engineer, or pharmacist. Now they are just beginning to find out that it will take a lot of hard work to reach their goal—symbols, problems, smells, instructions, and their bewildered minds set up a resistance.

It does not take long for any bright freshman to learn that there is a slick way out of laboratory work. While the instructor is at the other end of the room, safely hidden behind the bottle racks, he pumps the "grind" beside him. "What are you supposed to find here? What is the answer to this problem?" The "grind" has studied it all out, and Bright Freshman writes the data in his notebook. The paradox of the lab notebook is that it may have all the right answers, while the freshman's head may have none. It is also quite possible to get a fair grade at the end of the year, and not have any idea of what it was really all about.

Many attempts have been made to solve this difficult problem. More and better laboratory manuals and objective tests have flooded us; finer and more expensive laboratories have been built; more and more push-button methods to make it easier for the student, and still they "hate chemistry." For the one and perfect solution there has never been a substitute: "Mark Hopkins on one end of the log, and the student on the other."

What then will put the plus in the teaching of chemistry laboratory? What will turn these indifferent freshmen into devoted chemists?

## THE TEACHER HIMSELF

Without a doubt, the real teaching of chemistry takes place in the laboratory under a consecrated teacher. There is no place here for the intellectually arrogant, know-it-all, untouchable, high-and-mighty professor, mentally locked up in his ivory tower of research. The teacher must enter the lab as eager and open-minded as the humblest student. Remember, the discovery of methyl amine took place in a demonstration mistake, when the instructor was trying to make ammonia for his class.

Putting the plus in chemistry teaching means putting the "teacher" back in "teaching." In the laboratory the instructor has a golden opportunity to help the student understand principles, acquire skills, learn how to protect himself, develop the scientific attitude and love for his subject. By his actions and the way he explains things, the teacher tells the student that he is interested in what he is doing and likes the laboratory work himself.

In addition, the instructor watches the reaction of the students, learning from their response what bores them and what makes their eyes sparkle with interest. It is quite possible to "work the socks off a student," and make him love it. Perhaps the teacher observes that when he himself has more to give, more is received. No teacher should go into the laboratory having prepared *just* the day's lesson. He should be so full of his subject that it radiates from him, to the illumination of the students. God help the man who teaches merely to make a living!

## LABORATORY DISCIPLINE

The next thing necessary for a successful chemistry laboratory is strict discipline. A few rules should be laid down at the beginning of each semester, and no exceptions made, unless in extreme cases. Here are a few examples:

(1) Keep desk and equipment clean and in order.

(2) Never carry chemicals from shelf to desk. Go to the shelf with suitable vessel, get material needed, and return to desk.

(3) Keep the chemicals on shelf orderly and stoppered, so the next person can find everything where it belongs and in good shape.

(4) If any bottle or chemical becomes low, call that fact to the attention of the teacher.

(5) Absolutely no fooling in the laboratory. It is a workshop, not a rumpus room.

(6) Read carefully all instructions on what to do in case of accident. Preparedness is the best insurance.

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[1] Presented as part of the Symposium on Putting the Plus into College Chemistry Teaching at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] Recipient of the 1953 James Flack Norris Award for "outstanding achievement in the teaching of chemistry," a scroll and $1000 awarded by the Northeastern Section of the American Chemical Society. Just before going to press we received notice of the sudden death of the author. The sense of loss which we feel is not only personal but on behalf of the whole chemical profession, which can ill afford to lose one of its outstanding teachers.

(7) Read laboratory assignment thoroughly before beginning experiment, and obey instructions. If you have ideas for improving it, consult instructor first.

### REKINDLING CURIOSITY

There is hardly anyone who hasn't been pestered by a little boy's questions. "Why does the moon shine?" "What makes sparks on the cat's back?" Little boys can ask questions that nobody can answer, and are often squelched because the adult doesn't know, or doesn't have the time or inclination to look it up. As the child grows, his curiosity is partly satisfied and goes to sleep, because there are so many other things that adults make him learn.

By the time he comes to college, the student assumes an air of boredom to cover up his immaturity. He has also learned enough of life so that he "knows it all." To break through this barrier the teacher has to be good. But what a joy it is to see that youthful curiosity rekindled and shining in the eyes! To hear questions like this: "How is the absolute potential of a metal determined?" "Why is it that protons in the nucleus of the atom do not repel each other?" Of course, only the exceptional freshmen will think like this. But if you are a good teacher, you can rouse the ordinary student to ask, "Why does the needle float on the water?" Then you are on the road toward rekindling that precious curiosity which produced the Pasteurs, Edisons, and Fords.

What methods can the teacher use to rekindle this curiosity?

(1) Allow the students to make up their own problems and solve each other's. If they do well, commend them.

(2) Suggest they make up their own experiments. Send them to the library to find complete instructions. Before starting work, they must write up the experiment completely in full detail, so that the rest of the class can safely carry it out. Praise them for work well done.

(3) Divide them into small groups with a leader, and rotate the leaders often. These groups can study the assignment together, or substitute similar original experiments, or decide upon a project to carry out. The teacher must be there at all times to hold them responsible for the work, and keep them in bounds. The projects and experiments can be circulated from group to group. Maybe a prize can be offered for the best experiment of the semester. Suggestions: the "Handbook of Chemistry" for their use, tickets to the theatre for the group, or the rest of the class giving the winners a picnic. These prizes are very stimulating.

In this method the instructor has an excellent opportunity to teach intellectual humility, without which nothing is really learned. Let the students understand by your attitude that nobody knows it all, not even the faculty, and that that which we do know is continually changing. There is much more to learn than we have yet discovered. Perhaps the lab manual is wrong. The only way to find out is to try it. Intellectual freedom, under laboratory discipline, will give the student a new sense of his own worth and self-respect to replace that veneer of boredom he once had. It might even inspire him to conquer new frontiers.

### THE TEACHER'S ATTITUDE TOWARD THE STUDENT

Is the student a person or a lab desk number? Singly or collectively, students are just as individual as the instructor himself. Is the teacher's door locked, or do the students feel free to come in at any time with a problem? The time to attack it is when it is hot. If students have to wait until it cools off, half the value is gone. Many deep questions burst out in informal group discussions. Many a "bull session" is three-fourths wasted, but it may lead up to the final one-fourth that is worth its weight in gold. A teacher needn't lower his dignity to be "one of the boys." Let your concern for their welfare radiate from you to them in such a way as to create confidence and respect in their minds and hearts.

This fellowship of mutual trust yields rich dividends. Often an instructor is puzzled by the sudden failure of a good student, and indirect methods of finding the reason reveal nothing. If this mutual trust relationship has been built up, the instructor will one day find the student standing beside his desk with a troubled face. It takes only a few of the teacher's kindly, discreet questions to open the boy's heart to pour out his trouble. It may be financial, it may be family sickness, perhaps a roommate problem, even girl or wife trouble.

### DON'T MAKE A STEP-CHILD OF THE LABORATORY

It is common practice to put graduate students in charge of laboratories, and the high-and-mighty professor never comes near the place or soils his hands. The principle of work that applies to machines applies also to laboratory work: you get out of it just about what you put into it. Depending upon the size of the class, there should be more than one instructor in the lab at the same time. For every 30 students, there should be one full-time instructor and two assistants. Of course the instructor's valuable time should not be wasted on bottle-filling, storeroom work, or cleaning. Student assistants can do this work with great benefit to themselves and the teaching staff. Most of my best boys served three years as lab assistants, and learned as much that way as from their own courses. But all their work must be under the close supervision of a full-time, interested teacher who is in the lab while it is in session, going from one student to the other with individual as well as group instruction.

I realize that such an arrangement is expensive, but if this one phase of chemistry laboratory teaching is carried out, all the other four will fall into line.

What is our object in teaching chemistry laboratory, anyway? Just to push students through the assembly line like a car or a refrigerator? No, what we really want is to develop trained men with the true scientific attitude to lead us through the Atomic Age, and the freshman lab is the place to catch them.

# THE EARLY HISTORY OF DETERGENT SUBSTANCES[1]

## *A Chapter in Babylonian Chemistry*

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THE study of organic chemistry in Babylonia presents numerous difficulties owing largely to the lack of artifacts of these substances. In the inorganic field, where samples are available for analysis, progress has been made particularly with newer metallographic and spectrographic methods, even though the ancient literature has often been neglected by the chemist. For the history of soap, however, it is necessary to rely entirely on literary sources which frequently offer many uncertainties both in translation and interpretation. As an aid, therefore, a method of backward extrapolation has been utilized in this investigation, beginning with the fairly well authenticated Latin and Greek sources and threading back through the Aramaic, Egyptian, and Akkadian to the Sumerian third millenium B.C.

Our knowledge of the manufacture of soap and other detergents in antiquity has until recently been clouded by the heavy authority of Greek and Roman classical writers. In the Odyssey, Homer relates that Nausicaa, daughter of the King of the Phaeacians, used only water to wash her nuptial garments (*1*):

> They seek the cisterns where Phaeacian dames
> Wash their fair garments in the limpid streams...
> Then emulous the royal robes they lave,
> And plunge the vestures in the cleansing wave.

Pliny (77 A.D.) (*2*) attributed the invention of soap to the Gauls, who used it to dye their hair red. It was made from beechwood ash and tallow from goats in two forms, soft and hard.

In Greco-Roman times the Greeks washed themselves by pouring water over their bodies. The *thermae* (public baths) of the Romans used pools of water, waist-high, at different temperatures. There is as yet no conclusive evidence that any other cleansing agent was used for bathing. In more northerly countries the steam bath was more popular in later times, just as it is today, with the cleansing action aided by beating the body with bundles of twigs of the beech or oak trees (*3*).

In pre-Christian and early Christian times, putrid urine was much used as a cleanser. Its effectiveness results from its content of ammonium carbonate which reacts with fats and oils in wool to produce a slight saponification. Urine was collected at street corners in ancient Rome from passers-by by the *fullones*. These became so prosperous that they were later taxed by the government (190 A.D.) (*4*).

Galen (129–99 A.D.) advocated the use of soap as a medicament and preventive. He distinguished between two types of soap, made by the Gauls and Germans, the latters' being preferred. Later on, a pomade, manufactured in the German town of Mattium and called Mattian balls, came into general use with the more affluent of Roman women (*5*). Soap in the form of balls was used until the nineteenth century in Europe and is still sold in that form in some parts of the Arabic Middle East.

The first definite mention of soap as a detergent used in processing of textiles has, for some time, been considered to be in the Papyrus Graecus Holmiensis (*6*) of the third or fourth century A.D. Evidence from Babylonian sources now proves this to be incorrect, as will be demonstrated further on. That soap and other detergents were in use in Egypt and much earlier in Sumer in the third millenium B.C. will be demonstrated by evidence from the ancient Near-Eastern literature.

### ORIGIN OF "SOAP"

Philological evidence as to the origin of soap is lacking. The words for soap in Arabic, Latin, Turkish, Greek, Persian, German, Old High and Middle High German, French, Finnish, Hungarian, Dutch, and English are all cognates and probably of the same origin. Words for soap are unknown in Sumerian and Akkadian. In hieroglyphic Egyptian *anzir* is used, while in Coptic *anchir* denotes soap (*7*). It is of interest that in Middle High German, *sīfen* is used to indicate a trickle of water, so that *seifen* in modern German, besides having the meaning of the verb "to soap," also is a metallurgical term used to signify the extraction of ore from sand with the aid of water.

Most peoples of the ancient Near East devoted a great deal of attention to cleanliness. This was particularly true of the Hittites, Hebrews, Ugarits, and the peoples of Sumer and Akkad. In fact, the latter possessed special buildings for washing purposes. In an almanac from Assur (*8*) a man is cautioned not to enter a laundry (*bit musati*) on the sixth and seventh

[1] Presented before the Division of History of Chemistry at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

days of the month of Teshrit, this being in a month of penance. The customs of ancient Egypt demanded that the people wash after as well as before a meal (*9*). The Egyptians were well acquainted with natron and clay or steatite as detergents. St. Jerome (*10*) (fourth century A.D.) related that *nitrum* (soda) was made in Egypt in Nitria by the drying of lakes by the solar heat and that it was employed as a detergent. To remove grease from clothing the Egyptians probably used natron or fuller's earth (*11*).

In the Berlin medical papyrus (*ca.* 1350 B.C.) a prescription includes natron and tallow (*12*). The Ebers papyrus, about 200 years earlier, has a number of recipes in which alkaline substances are boiled together with oils and fats to yield soaps and plasters (*13*).

Simple detergents commonly used in ancient Babylonia were alkalies, clays and earths, or resins, with the first predominating by far. Alkaline substances were generally procured from wood or plant ash in Mesopotamia, although it is possible that a very small amount was obtained from other sources. The Hittites, in a text of *ca.* 1300 B.C., used a "salt," possibly soda, and another alkali from plants, for washing the hands in a religious ceremony. They may have obtained their alkali from Lake Van, of which Strabon (*14*) (d. 20 A.D.) remarked that it contained soda which had good detersive properties. Alum was also used to wash clothing and is mentioned in the Babylonian Talmud a number of times (*15*). Although the Talmud was canonized about 500 A.D., it drew to a large extent on Babylonian technology of the first millenium B.C. Fuller's earth (*16*) is also mentioned in the Talmud as a detergent. The cinders of *borith* (*17*) mentioned in the Bible are probably potash (*18, 19*), soda, or a mixture of these carbonates together with other salt impurities. In the Revised Standard Version, Jer. 2:22, *nether* is translated as lye and *borith* as soap:

> Though you wash yourself with lye and use much soap
> The stain of your guilt is before me....

Luther considered *nether* to be chalk since it effervesced with vinegar (*20*). *Natar,* to effervesce, and *nether* may be cognates (*21*).

## SOAP PLANTS

Although the saponins are of widespread occurrence, there is no concrete evidence that the ancients made aqueous extracts of plants for cleansing purposes. This is in spite of the fact that aqueous extraction was well known and had been brought to a high perfection in perfume manufacturing in the second millenium B.C. (*22*).

In regard to alkaline detergents in Babylonia, the evidence is now complete that soda and potash were used from plant and wood ash as the most common washing substances in the household, for the cleansing of both clothes and the body. Furthermore, soap plants are found in great abundance in the Near East. The soapwort is a very common sapless shrub growing between Koum and Teheran (*23*). *Salsola kali,* the soda plant, grows near the Dead Sea today and is common in Syria, Egypt, and Arabia. Egyptian soda and potash, to some extent in modern times, is made from the ash of *Mesembrianthemum copticum* and *M. nodiflorum* (*24*). The horned alkali plant, *Salicornia,* or *kali* as it is called by the Arabs, found in the deserts east of Palmyra, El-'Asha, and Nejd, is still burned to an ash for its alkali. The horned alkali plant has thus been used for over 5000 years for this purpose. It occurs in the most ancient medical text known, in a prescription for the preparation of a detersive medicine for a sick person. In modern India the *Salicornia* plants are burned in pits until the alkaline substances fuse and collect at the bottom, forming what is known as "barilla" (*25*).

In ancient Babylonia many other plants were used for their alkaline substances. In an Akkadian text belonging to a private citizen in the time of Asurbanipal (*26*) (seventh century B.C.), the tamarisk, date palm, pine cone, and *mastakal* plant are used as detergents. "May the tamarisk, whereof the tops grow high, cleanse me; may the date palm, which faces every wind, free me; may the *mastakal* plant, which fills the earth, clean me; may the pine cone, which is full of seed corns, free me." The *mastakal* plant, evidently a very abundant one, is still unidentified. Further on in the same tablet: "I carry a container with an aqueous solution of *mastakal* plant to the gods of the heavens. As I would bring forth to you for your purification, so will you cleanse me." Rue, another washing plant, was in wide use in ancient times just as it is today near Carchemish, where women burn it to obtain the ash (*27*).

An old Sumerian tablet found in the Hittite capital of Boghazkoi relates the use of soda for cleansing the body: "With water I bathed myself. With soda I cleansed myself. With soda from a shiny basin I purified myself. With pure oil from the basin I beautified myself. With the dress of heavenly kingship I clothed myself" (*28*). This quotation shows the steps in their order of washing with water, then with soda, and finally with oil.

Although the washing plants of Babylonia were very numerous and in widespread use, there is no evidence as yet that the alkaline substances obtained from their ash were causticized. Nor has detailed evidence been discovered yet as to the exact method of working the plants for the extraction of alkali. Judging by the processes described in the extraction of essential oils from plants, there is no doubt that the Babylonians had developed to a fine degree their operations with alkali plants. In more modern times the operations which resemble those probably used by the Babylonians include the slow combustion or incineration of the dried plants, then a leaching or washing of the ash followed by evaporation until a salt cake forms on the

sides of the vessel, and then calcination of the crude product to drive off the water and destroy organic substances. These detailed operations, it may be conjectured, were probably in use for the manufacture of soda or potash for the use of the priesthood or royalty. For the common household chores the ash was probably stirred in water and the solution filtered before using to remove the insoluble impurities. The method of containing the ash in a cloth bag which was immersed in the wash water was in use up until the nineteenth century, when soap finally became cheap enough to displace the alkali plant ash in the European home.

## MEDICAL IMPLICATIONS

Soap in Babylonian and Egyptian literature is found mainly in connection with medical writings. Very early, soap was found to be of value as a medicament. Its use has continued up to the present day in medicine, where it is now used for scabies, chiggers, in prophylaxis of venereal diseases, prevention of industrial dermatoses and infection, wounds, and burns (*29*).

In a medical tablet of the first millenium B.C., in Akkadian, a soap is made up by the pharmacist as follows. "A vessel is filled with water . . . and tamarisk, soapwort, 'reed for plaiting,' *Salicornia* alkali and 'mixed' beer put therein, and then a ring of *sariru*-gold; the man to be given pure water to drink, and then the solution thus prepared is to be poured over him; then turmeric root is to be pulled up, pure salt and pure alkali pounded, fat of a crane . . . added to this, and the patient's body rubbed seven times with it" (*30*).

In another tablet of this period a ritual cleansing recipe is given, where in a large kiln vessel are placed *Salicornia* alkali, salt, *mastakal* (alkali plant), various oils, fat of a cow, white lead, and other substances. This probably formed some type of metallic soap or plaster.

The *Ricinus* plant from which castor oil is derived is today very common in Mesopotamia.[2] It is therefore not surprising to find this plant used in the preparation of soaps, particularly since castor oil does not require much heat for saponification with alkali. In a prescription of the seventh century B.C., soap made from castor oil and horned alkali is used, together with other drugs, as a mouth cleanser, in enemata, and also to wash the head (*31*). It may seem odd at first glance that castor oil is used in a mouth wash, but it should be remembered that in the Near East it is considered to be a delicacy.

From the library of Asurbanipal (seventh century B.C.), we have the prescription for the sprinkling of a patient with a solution that seems to be a resin and oil soap combined. In this case, *mastakal* ash, "small palm," pine resin, and *Juniperus oxycedrus* are used to make up the soap. This prescription recalls to mind a "sapo tartareus," a medicated soap made of turpentine oil and vegetable alkali which was popular in London about 1685 and highly recommended for treatment of gravel.

Sulfur ointment was known in Assyrian times. A typical cleansing formula was as follows: "Take turpentine, sulfur, horned alkali and put in water, then oil and spittle are poured thereon forming an ointment" (*32*). The purpose of the turpentine may be to take the sulfur into solution.

Another recipe is a sulfur ointment for the eyes. It makes use of saltpeter, iron sulfate, *Salicornia* alkali, fir turpentine, niter, *Lepidium*, sulfur, ox-fat, and other substances (*33*).

In the Sumerian literature a cylinder of the third millenium B.C. gives water, alkali, and oil as the ingredients of a soap recipe (*34*). A very interesting recipe for soap is given in a text dating back to the third Dynasty of Ur (*ca.* 2200 B.C.). The text is rare for its quantitative directions and specifies 1 *qa* of oil and $5^1/_2$ *qa* of alkali, the latter probably in the form of ash. Another soap recipe used in the washing of wool includes oil, *himetu-ghee*, wood ash, and other substances (*35*).

A Sumerian medical tablet of this period describes a prescription which includes *Salicornia fruticosa* (alkali plant), salt, cassia oil, and powdered asafoetida, together with other substances. These are all kneaded together. Fine beer and boiling water are then poured thereon. The solution is then sprinkled upon the patient, followed by a rubbing with tree oil. In the same tablet another soap recipe directs the pharmacist to pulverize fir and skin of a water-snake, then add root of myrtle, alkali ash, barley, powdered fir resin, *kusibu* plant, and water, then boil. This is filtered and then the filtrate is poured upon the patient. Tree oil is then rubbed upon him (*36*).

It is apparent from the soap formulas described above that a true soap using caustic alkali was probably not produced in antiquity. Rather do the soaps resemble those produced in some parts of the world in the present day, known as cold or semiboiled soaps, in which the substances including the glycerin and water remain in the congealed or liquid state. The cold or semiboiled process is of course applicable only to the manufacture of soaps from readily saponifiable oils. Castor oil would easily fit this requirement. There is some evidence that the soap was separated from the glycerin.

## RESIN SOAPS

The recipes described earlier give good reason to believe that the ancients were acquainted with resin soaps. These are compounds of soda or potash with the complex abietic acids found in coniferous resins. In the modern soap industry resin is used, together with fats, in a number of various types of soap. Resins saponify readily and rapidly and their soaps have a high solubility and good lather (*37*).

[2] Sumerian *AG-PAR*, hiero-Egypt. *K3K3*, Gr. *kiki*, Heb. *qiqayon*, Arab. *hirwa'*, Syr. *qerda*, Sanskrit *eranda*. There is no cognate to any of these terms in Akkadian for the *Ricinus* plant.

Carbonate saponification practiced by the Babylonians is an operation which must be carefully regulated to prevent overrunning owing to evolution of carbon dioxide in the boiling process. No mention is made in our texts of the details of manufacture, and so we are left in the dark as to the preventive steps taken in antiquity.

The texts definitely indicate that "salting out" was practiced 5000 years ago to separate the soap from the glycerin, excess of water, and impurities. Unfortunately, the highly abbreviated character of the prescriptions does not give us much information on this point, except that in two prescriptions of the Sumerian tablet, now in the University Museum, the pharmacist is directed to filter the solution. This probably refers to the soap solution.

In conclusion, soap has been manufactured for over 5000 years. Resin and sulfur soaps were known at an early date. The earliest soaps known were made for medical purposes and for the washing of wool but not for general detersive use. Evidence has been adduced to indicate that "salting out" was in use in early Sumerian times. Soda and potash from plant ash were the most common washing agents from early antiquity to the middle of the nineteenth century A.D. Other substances played a relatively minor role in the ancient history of detergents.

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# INSTRUCTING THE REPORT AUTHOR[1]

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"SCIENTISTS can't write." This platitude is voiced in some part of the scientific world every day. The very volume of scientific writing now appearing apparently belies this statement. The technical journals are swamped with manuscripts written by thousands of technical people. Witness the program of a meeting of the American Chemical Society. Hundreds of papers written by chemists are given, and thousands of people come to listen to scientists who, it is said, can't write.

Yet the clamor is still heard, unhushed by this evidence of quantity. The critics of scientific writing present their own evidence. Walter and Mills[3] of the University of Texas show the demand for technical editors throughout American industry to write, rewrite, criticize, and correct. The cry is not for increased quantity but for improved quality.

Specifically, the usual scientist lacks the training to write properly. He was never taught in his scientific training how to reduce an idea to written words. He is unaware of the techniques for presenting data in a manner compatible with their value. Finally, he is verbose. Concise writing has magic in it. His windiness has bred the storm of protest.

On-the-job training courses were invented to attack problems of this nature, problems avoided or neglected in the formal, academic institutions, problems for which there is no answer book. An on-the-job training course lends itself admirably to the problem of training report writers. Industry can train its scientists to write properly. Why not train *your* scientists to do so?

Mound Laboratory, with which I was associated, is a Monsanto organization operated for the Atomic Energy Commission. Naturally, the scientists at Mound write a large number of reports, and we have an ever-increasing number of journal publications to our credit. As more reports were written, the need was felt for a training program to increase the quality of the scientific writing at Mound. A training program was, therefore, planned and conducted for 125 scientific report authors.

This program was, of course, tailored to the needs of our authors and the needs of Mound Laboratory. But a similar program can be conducted at your place of business, provided you have two qualifications: a cooperative, or even an aroused, management, and the strength of your own convictions.

Use adult training methods. When there are facts to be imparted, lecture. When the application of techniques is brought up, discuss. When intentions are the subject, encourage debate.

Use the modern techniques available for training. Use slides, turnover charts, outlines, manuals, and other visual aids. Record as much of the sessions as practical and distribute summaries to those who attended, as well as to management.

Things happen when a collection of good scientific talent takes part in a report training program. Ideas you have never thought of come up. Hidden talent is discovered. Understanding of the reader's needs is fostered in these authors.

When the program is over, the authors show an increased willingness to write reports. The very enthusiasm generated in the authors at the conclusion of the program will justify the time of preparation. More efficient writing of better quality reports results, and management finds itself better informed on the progress and achievements of its employees.

The questions most often asked by authors provide a good basis upon which to develop a training program. Here is a list of the basic questions of our program in the order of attack:

(1) To whom are we writing?
(2) How can we best organize our information?
(3) How should we present our data?
(4) How do we write a good abstract?

Let us examine the first question. Who *are* the readers of the reports at your place? Our readers were found to belong to four classes: (1) members of immediate supervision; (2) top management; (3) other scientists who were not administratively or geographically associated but who had a scientific interest in our work; and (4) the author himself and his co-workers.

Find a representative of each class of your readers and ask him to lecture briefly on what he wants, needs, and looks for in a report that comes to his attention. Give each representative ten minutes.

We found that immediate supervision used reports to help judge their man. Supervisors frequently served as critics of reports, or used them as a basis for their own reports. They also relied upon reports for a complete and accurate record of progress or accomplishment.

Top management, being remote from the actual work, found reports indispensable for the evaluation of progress and for deciding on the future course of the Laboratory's research. Brevity and accuracy were empha-

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[3] WALTER, J. A., AND G. MILLS, *Chem. Eng.*, **60**, 250 (August, 1953).

sized by management. It was pointed out here that frequently the only product management gets for its research dollar is a report.

The busy scientist at another laboratory wants a report to be clear and unambiguous and to contain sufficient detail to permit repetition. Accuracy is of particular importance. Subtle errors, typographical or otherwise, may cost him much time and money in an attempt to duplicate. The misplaced decimal point and the omission of the word "not" are examples of subtle errors. Obvious errors, grammatical or otherwise, create a sense of disrespect for the quality of the original research. Improperly cited references, for example, are most annoying.

The author himself has much to gain from a properly prepared paper. As an author he builds his professional reputation on his writings. His list of reports and publications are his record of accomplishment. But of more immediate gain as a reader of his own draft is the fact that he frequently can detect flaws in his own research logic, significant gaps in his data, and, many times, fruitful avenues for new research that did not occur to him as he concerned himself with the intricate details of the problem at hand. Writing a report lends perspective to the laboratory work. A report in this sense is a valuable research tool. Furthermore, an author's writing is made easier by his continued writing.

The question of readership is now at least partially resolved. The author has some idea of what is expected.

Question 2, relating to the organization of information, did not lend itself to such an expository presentation. Organizing information for a technical report is not a stereotyped procedure. A properly led discussion of this question seemed to be the best approach. Since a discussion is cumbersome in a group of 125, many smaller groups of about 15 were formed. The members of the groups were selected so as to include a cross section of the Laboratory's research program in each group.

During these discussions, many suggestions on how to organize information were submitted.

The following list contains a few of the many points suggested by the authors while discussing this problem of organizing their presentation.

(1) Find a quiet place to write.
(2) Make work schedule for writing.
(3) Prepare and assemble data.
(4) Make outline.
(5) Interpret data before writing report.
(6) Prepare the reader with problem and its justification in the introduction.
(7) Define terms carefully.
(8) Allow manuscript to "cool" before attempting to revise.
(9) Determine your readership.
(10) Assemble and reread bibliography.

A sure-fire means of creating a discussion is to present a portion of a particularly bad report for criticism by the group. Use a small segment that is quickly read when shown on a screen. Invite the group to criticize. Of course, the author should not be present. Indeed, it is preferable that he not be even associated with your organization any longer.

When the criticisms are all in, ask the group for means of avoiding each of these errors. Their answers will reveal to them that the average technical man has the innate ability to write well, if he will. The job of the report training program director is to point up this fact, to clear away the mystical ghosts about writing, and to challenge each author with the responsibility for the quality of his own writing.

The third session of the report construction training program was devoted to problems of organizing data and to the functions of the various types of illustration. For the purpose of our program, we included tables along with graphs, drawings, and photographs as illustrations. Find out what the authors think of illustrations. Are they really useful in a report? If so, what are the uses? Our authors came up with 30 different and distinct functions of illustrations. Illustrations provide continuity of data, perspective, emphasis, a common language throughout the world, and a more permanent impression on the reader than does the written word. They show subtle relationships, trends, details not easily described in English, and many other things.

Such a review of means for presenting data broadens the outlook of every writer present, and suggests possibilities that have never occurred to them before. We went further into illustrations than just a casual discussion of utility. Each type of illustration has its characteristic uses. When does one use a table, a graph, or a photograph? What is involved in making the right decision? The table contains some of the pertinent answers.

It was brought out that there are many types of

**The Functions of Illustrations**

*Characteristic uses of drawings*
(1) Describe equipment tolerances
(2) Permit transparent views
(3) Show specific details
(4) Allow selectivity

*Characteristic uses of graphs*
(1) Show trends
(2) Provide rapid comparison
(3) Allow graphic solutions
(4) Permit condensation of data
(5) Allow reader summaries
(6) Show weak points of data

*Characteristic uses of photographs*
(1) Show position of equipment
(2) Show third dimension
(3) Are adaptable to exploded views
(4) Show real results
(5) Show techniques and problems involved
(6) Establish authenticity
(7) Allow rapid reproduction of data

*Characteristic uses of tables*
(1) Show a multitude of variables
(2) Useful for unrelated data
(3) Can show the importance of a number
(4) Show all data

curves or graphs. Several types were shown and the individual utility of each was discussed. A bar graph permits grouping of data, a smooth curve through the data allows the effect of statistically treating the data to be shown with the raw data, etc. A wide variety of applications for an equally wide variety of graphs shows that reports are not stereotyped but permit a wide choice of presentation methods.

The fourth and final one-hour session of the training program at Mound Laboratory was devoted to a lecture and question period on the preparation of abstracts. We were fortunate to have a professional abstractor on our staff. However, most organizations have in them members of Dr. Crane's family of Chemical Abstractors. Careful choice of one of these men will serve admirably to provide an authority on how to write a good abstract.

Essentially, a good abstract comprises the essential qualities of the larger report in a condensed form. Clear, well-phrased, short sentences should be used to inform the reader as briefly as possible of specific information. Tell the reader why, how, and what was accomplished.

When your program is finished, there is still work to be done. It is of critical importance that the results of the discussions, the arguments and conclusions established, and the high points of the program be put into writing and sent immediately to each author in attendance and to each member of management concerned. This follow-up serves the dual purpose of the textbook and lecture notes so familiar and necessary to your university-trained audience. These people need a piece of paper for reference. The next report that they will write may be weeks or months away. Also, to keep the discussion alive, send out this follow-up.

A well presented on-the-job report training program will arouse the enthusiasm of those in attendance for writing, and the improved reports that result will bring smiles of appreciation from management.

# THE ZERO OXIDATION STATE

**ERVIN COLTON**
University of Illinois, Urbana, Illinois

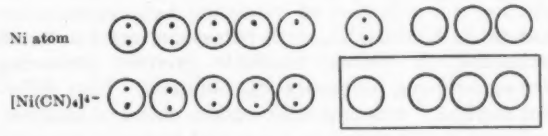
ONE of the most unusual oxidation states is the zero-valent state found in metal carbonyls, in complex cyanides, and recently in interesting ammine and isonitrile complexes. The carbonyls represent a large and fascinating branch of inorganic chemistry, but they will not be discussed here as they have been reviewed adequately elsewhere (*1*, *2*). Rather, examples of the other classes of compounds containing transition elements in the zero oxidation state will be described.

The reduction of the complex cyanides of certain transition metals by potassium metal in liquid ammonia leads to interesting products in which the central atom of the complex ion exhibits an *effective atomic number* equal to the atomic number of the inert gas at the end of the period in which the element is placed in the periodic classification (*3*).

Eastes and Burgess (*4*) obtained a bulky yellow precipitate by reaction of an excess of potassium with potassium tetracyanonickelate(II), $K_2Ni(CN)_4$, in liquid ammonia. When freed of ammonia the product was copper colored and extremely unstable in air and in oxygen, turning black on exposure. A deep red solution resulted upon dissolving the reduction product in water. The red aqueous solution exhibited all the properties of a solution of $K_2Ni(CN)_3$. Analysis of the unusual product, taking nickel to be unity, showed the constituents, K, Ni, and CN to be present in the ratio of 3.977:1.000:3.863. Thus the empirical formula $K_4Ni(CN)_4$ was assigned.

$$K_2Ni(CN)_4 + 2K \rightarrow K_4Ni(CN)_4$$

This complex can be regarded as an analogue of the carbonyl $Ni(CO)_4$, in which the neutral carbon monoxide groups have been replaced by four monovalent cyanogen ions. Since studies by means of electron diffraction (*5*) and by means of infrared (*6*) have shown that $Ni(CO)_4$ is best described as a tetrahedral structure, it seems reasonable to believe that the $[Ni(CN)_4]^{4-}$ ion also would exhibit this same configuration.

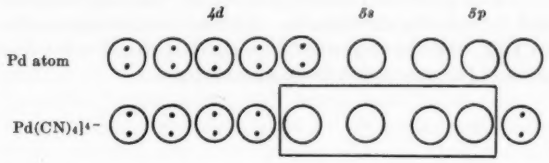



A similar zero state has been observed with palladium. Burbage and Fernelius (*7*) reacted potassium metal and potassium tetracyanopalladate(II),

$K_2Pd(CN)_4$, in liquid ammonia and observed the formation of a moderately soluble white precipitate which was stable for at least six hours in liquid ammonia at $-33°$, and for approximately two hours in an ammonia atmosphere at room temperature. Total analysis and reacting ratios of potassium to starting material indicate the reaction product to be potassium tetracyanopalladate(0), $K_4Pd(CN)_4$.

$$K_2Pd(CN)_4 + 2K \rightarrow K_4Pd(CN)_4$$

Here, as in the previous case with nickel, the palladium exhibits an oxidation state of zero. The $[PdCl_4]^{2-}$ ion has been shown by X-ray examinations to be planar (*8*). It would thus appear that the $[Pd(CN)_4]^{4-}$ ion should also exhibit the same configuration.

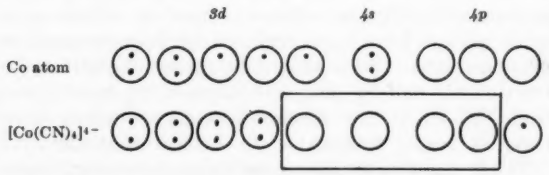



A complex containing cobalt(0) has also been described (*9*). Finely divided potassium hexacyanocobaltate(III), $K_3Co(CN)_6$, was suspended in liquid ammonia and treated with metallic potassium.

$$K_3Co(CN)_6 + 3K \rightarrow K_4Co(CN)_4 + 2KCN$$

The brown-violet product was finely crystalline and sensitive to air and evolved oxygen on contact with water. The reducing equivalent of the new compound was determined by reaction with potassium ferricyanide solution.

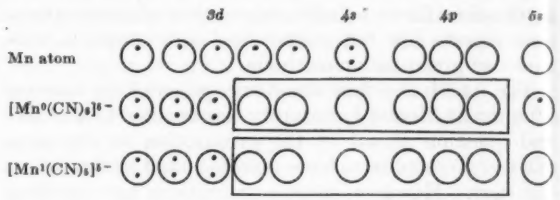
No magnetic data were presented, but it appears that the resulting complex should be paramagnetic, corresponding to the presence of one unpaired electron. By analogy with the planar configurations established for the platinum-nickel and copper-silver group of metals in their bivalent state (*10*), it may be expected that the complex would possess a planar structure.




Recently Christensen, Kleinberg, and Davidson (*11*) studied the reduction of potassium hexacyanomanganate(III), $K_3Mn(CN)_6$, with potassium metal in liquid ammonia. A yellow, insoluble product possessing strong reducing properties was obtained. Four different methods—reacting ratio studies, chemical analyses, reducing power determinations, and magnetic measurements—show the product to contain manganese in a mean oxidation state of $+1/2$.

$$2K_3Mn(CN)_6 + 5K \rightarrow K_5Mn(CN)_6 + K_4Mn(CN)_6$$

The composition of the product is represented as $K_5Mn(CN)_6 \cdot K_6Mn(CN)_6 \cdot 2NH_3$. The magnetic moment was found to be 1.25 Bohr magnetons, compared to a calculated value of 1.73 for one unpaired electron.



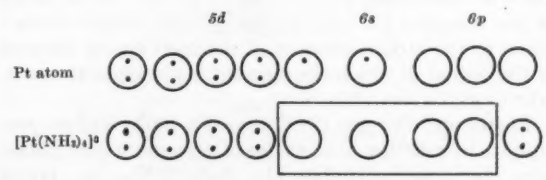

It is seen that a complex containing manganese in the zero oxidation state would contain one unpaired electron and would presumably be octahedral, having $d^2sp^3$ bonding. The complex with unipositive manganese would be diamagnetic and would be octahedral also. By assuming a mixture of 40 mole per cent of manganese(0) and 60 mole per cent of manganese(I), the investigators were able to account for the observed moment.

Potassium tetracyanoplatinate(II), $K_2Pt(CN)_4$, reacts with a solution of potassium in liquid ammonia, but the complete characterization of the product is handicapped by the relative insolubility of the starting material and the marked evolution of hydrogen. Addition of potassium to a solution of $K_2Pt(CN)_4 + KNH_2$ resulted in very little hydrogen evolution. The reacting ratios of K to $K_2Pt(CN)_4$ of 2.057 to 1 suggest that the white precipitate is potassium tetracyanoplatinate(0), $K_4Pt(CN)_4$, but the theoretical values and the analytical results are not in good agreement (*7*).

More recent evidence for the existence of a complex of platinum(0) comes from the studies of Watt, Walling, and Mayfield (*12*) who reduced tetrammineplatinum(II) bromide, $[Pt(NH_3)_4]Br_2$, with potassium in liquid ammonia. The yellowish-white product yielded only elemental platinum and ammonia upon thermal decomposition, which occurs at or below 25°.

$$[Pt(NH_3)_4]^{2+} + 2Br^- + 2K^+ + 2e^- \rightarrow 2KBr + [Pt(NH_3)_4]^0$$

Since the tetrammineplatinum(II) ion has been shown to be of the $dsp^2$ type (*13*), it is reasonable to ascribe the planar configuration to the $[Pt(NH_3)_4]^0$ species also.




A similar zerovalent iridium complex is also reported by Watt and Mayfield (*14*). The reduction of bromopentammineiridium(III) bromide, $[Ir(NH_3)_5Br]Br_2$, with potassium in liquid ammonia results in the formation of an insoluble pale yellow solid which yields only

ammonia and iridium upon thermal decomposition at 92–93°.

$$[Ir(NH_3)_5Br]^{2+} + 2Br^- + 3K^+ + 3e^- \rightarrow [Ir(NH_3)_5]^0 + 3KBr$$

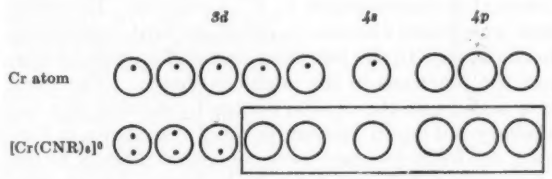
Magnetic measurements indicate that the product is diamagnetic although this result is not yet conclusive.

Potassium hexacyanochromate(III), $K_3Cr(CN)_6$, has been reduced with potassium in liquid ammonia, but the investigators were unable to find any consistency either in the reacting ratios or in the analysis of the brown precipitate (*7*). An uncompleted reinvestigation of the reduced product pointed to the existence of Cr(I) in the brown material (*15*).

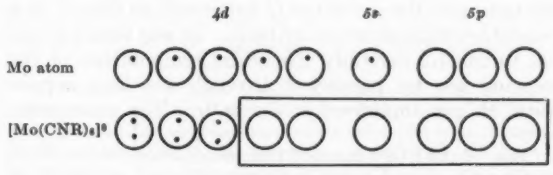
More conclusive evidence for the existence of a zerovalent chromium complex comes from the work of Malatesta, Sacco, and Ghielmi (*16*) who treated chromium(II) acetate with organic isonitriles and obtained a red product of the general formula $Cr(CNR)_6$.

$$3Cr^{++} + 18RNC \rightarrow Cr(CNR)_6 + 2Cr(CNR)_6^{3+}$$

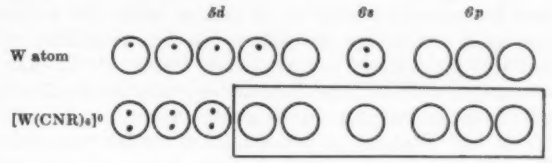
The product was found to be diamagnetic. An examination of the electronic configuration of chromium reveals that the addition of six neutral groups would result in the formation of an octahedral complex, $d^2sp^3$, in which the chromium atom would exhibit an *effective atomic number* of 36, corresponding to the atomic number of krypton.




An analogous isonitrile complex has been prepared with molybdenum (*17*) by reaction of an alcoholic solution of molybdenum(III) chloride and excess isonitrile in the presence of powdered magnesium. The product, $Mo(CNR)_6$, is red, crystalline, and slightly magnetic, the slight degree of magnetism being ascribed to decomposition of the complex. The structure of the product may be expected to be octahedral.




Tungsten, also, has been shown to form complexes with isonitriles (*18*) by reaction of tungsten(VI) chloride and the isonitrile in alcoholic solution in the presence of powdered magnesium. The resulting complex, $W(CNR)_6$, is red and crystalline, and possesses a slight degree of magnetism owing to some decomposition of the product. By analogy with the complexes of chromium(0) and molybdenum(0), it seems reasonable that the tungsten(0) complex would also possess an octahedral configuration.




An isonitrile complex of nickel(0) is known also (*19*).

## ACKNOWLEDGMENT

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# MEASUREMENT OF THE JOULE-THOMSON COEFFICIENT[1]

## *A Laboratory Experiment*

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SINCE the properties of gases, real and ideal, are used extensively as illustrations in elementary thermodynamics, there has seemed to be a need for more quantitative laboratory experiments involving gases. Measuring the Joule-Thomson coefficient, $\mu$, of a gas would seem to be the most practical and direct method of studying deviations of a real gas from ideal behavior, and of illustrating some of the simple thermodynamic relationships. The simple apparatus described below was assembled in a relatively short time from items usually available in a college laboratory, the only expensive item being a sensitive, low-resistance, d.-c. galvanometer.[2] For $CO_2$ and $N_2$, values of $\mu$ have been obtained which agree with the accepted values to within the experimental uncertainty of $\pm 3$ per cent of the present results. It is interesting to note that the original "porous plug" experiments of Joule and Thomson (*1*), which were carried out exactly 100 years ago, yielded remarkably accurate results for the same gases. It is a worth-while experience for students to read the original papers of Joule and Thomson; the two scientists become much less names in a textbook and much more the great experimentalists and thinkers who helped to build the science of thermodynamics. In what follows it is assumed that the reader is familiar with the nature of the "porous plug" experiment and the basic principles involved.[3]

### DESCRIPTION OF THE EXPERIMENT

The apparatus used is shown schematically in Figures 1 and 2. The porous plug consists of a fine-grained, sintered, Pyrex glass disc $A$ sealed into a tube $B$ of 30-mm. diameter.[4] Gas at the higher pressure, $P_2$ (say 1 atm. $< P_2 <$ 2 atm.) flows in at $C$, passes through the plug $A$, and finally passes out to the atmosphere through the holes $D$[5] in the outer jacket $E$, which serves mainly to minimize the heat transfer through the walls of $B$. The outer jacket is supported by asbestos or cork rings (cross-hatched) and serves also to support the lower thermocouple.

The difference in temperature, $\Delta T$, between the high pressure gas directly above the plug $A$ and the low pressure gas below is measured by a single-junction copper-Constantan thermocouple $F$, $F'$[6] as shown. The wires used were small enough to minimize heat conduction down the wire to the junctions, but stiff enough to support the junctions in the positions shown. The wires were sealed into the capillary tubes by sucking into the capillary hot liquid Apiezon W wax.[7] As shown in Figure 1, the leads (copper) were connected directly to the galvanometer,[2] the reading of which was directly proportional to $\Delta T$. The proportionality constant was obtained by direct calibration against Beckmann thermometers (before assembly) and also from accurate knowledge of the resistances in the circuit. The galvanometer sensitivity was reduced when necessary by using an accurate resistance box as a shunt. With no shunt one mm. deflection corresponded to 0.0053°C. difference in temperature.

The whole assembly shown in Figure 2 was packed into the container, $G$, with vermiculite (for thermal insulation) and the container $G$ immersed, as shown, in a constant-temperature water bath. It was found essential to control carefully the initial temperature of the entering gas by passing it through the long copper spiral $H$, also immersed in the bath. The gases came

[1] These experiments were carried out mainly in the physical chemistry department of the Massachusetts Institute of Technology, Cambridge, Massachusetts.

[2] A Leeds and Northrup No. 2430-D d.-c. galvanometer was used. The resistance was rather high, but actually the voltage sensitivity is the important factor. The characteristics were: current sensitivity, 0.000411 amp./mm. deflection; resistance, 534 ohms.

[3] See any good textbook of physical chemistry or thermodynamics, *e. g.*, GLASSTONE, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, 1946, pp. 286 and 292.

[4] This ($A$ and $B$) is a standard item manufactured by the Corning Glass Co., item No. 39570, diameter 30 mm., porosity F, in Catalogue No. LB-31.

[5] There are six holes equally spaced around the tube at the position shown.

[6] No. 36 insulated copper wire and No. 30 insulated Constantan wire.

[7] A low vapor pressure sealing wax obtainable from J. G. Biddle Co., Philadelphia, Pennsylvania.

from commercial cylinders and were cooled considerably[8] on passing through the pressure regulator attached to the cylinder. The high pressure is maintained sufficiently constant by using the standard commercial pressure regulators, and the difference in pressure, $\Delta P$, was measured accurately by connecting the high pressure side to a mercury manometer open to the atmosphere on the low pressure side. The apparatus is designed so that no significant differences in pressure exist except across the plug $A$.

After the system has come to thermal equilibrium (no gas flowing), the gas flow is started and the high pressure adjusted to a given value. On the average it was necessary to take readings of $\Delta T$ over a period of about 30 minutes under constant pressure conditions to make sure that $\Delta T$ had become sufficiently independent of time (say, less than 0.01° change in five minutes). In this manner values of $\Delta T$ corresponding to various high pressures (therefore $\Delta P$'s) are obtained. Since $\mu$ is to a good approximation independent of pressure over a range of a few atmospheres, a plot of $\Delta T$ against $\Delta P$ should be a straight line passing through the origin and with the slope $\mu$; for a single determination we can write $\mu = \Delta T/\Delta P$. Figure 3 shows data obtained by us and by students in the undergraduate physical chemistry laboratory at Bryn Mawr College for $CO_2$ and $N_2$ and also by Joule and Thomson for $CO_2$ and air[9] for comparison. Our values for 20°C. of 1.06 ± 0.03 for $CO_2$ and 0.23 ± 0.01 deg./atm. for $N_2$ compare satisfactorily with the accepted values (*2,3*) of 1.10 for $CO_2$ and 0.23 for $N_2$ under the same conditions of pressure and temperature. The uncertainties are estimated from those in the individual $\Delta T$ measurements.

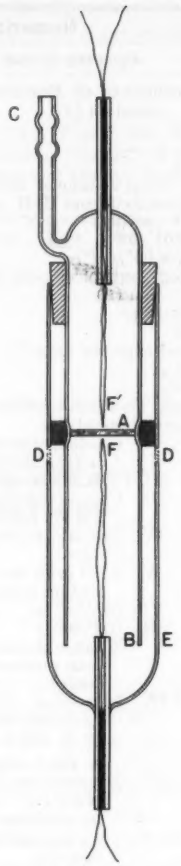


**Figure 1**

*A*, Porous (sintered glass) plug
*B*, Inner glass tube
*C*, Inlet for high-pressure gas
*D*, Outlets for low-pressure gas
*E*, Outer glass tube
*F*, Thermocouple junctions

It seems clear that the apparatus described represents only one of a number of possible (and equally simple) designs, many of which would give results as good or better than those presented. In addition to Joule and Thomson's paper, those of Roebuck and collaborators (*4–7*) can be consulted in designing an apparatus. The sources of systematic experimental errors boil down mainly to unwanted transfers of heat by radiation and by conduction across the plug and walls of the vessel and down the thermocouple wires. For the apparatus described above, the error in temperature measurement owing to the nonrandomness of the molecular velocities introduced by the bulk flow of the gas can be shown easily to be negligibly small.[10] If mercury-in-glass thermometers are used, a method similar to that of Joule and Thomson (*1*) could be used to avoid errors resulting from the effect of pressure on the thermometer readings.

## TREATMENT OF THE DATA

Since $\mu$ values for a gas provide quantitative information concerning the gas imperfections, it is interesting, as an exercise, to see how $\mu$ is related to other properties of the gas and of the individual gas molecules. Below are listed some suggestions for calculations of possible

[8] In the case of $CO_2$ the Joule-Thomson cooling in the pressure regulator is so great that, over a period of time, heat must be supplied to the regulator to prevent solid $CO_2$ from plugging the throttling valve in the regulator. Recall the well known demonstration of making solid $CO_2$ "snow" by the rapid expansion from a cylinder through a porous bag.

[9] Oxygen and air have a Joule-Thomson coefficient very close to that of nitrogen at low pressures; actually Joule and Thomson used a mixture of $CO_2$ and air (obtained from fermentation!) and calculated the value of $\mu$ for pure $CO_2$ by using a somewhat arbitrary assumption concerning mixtures of gases.

[10] The extra kinetic energy corresponding to the component of velocity introduced by the bulk (Poiseuille) flow of the gas is very small compared to the average kinetic energy of random motion.

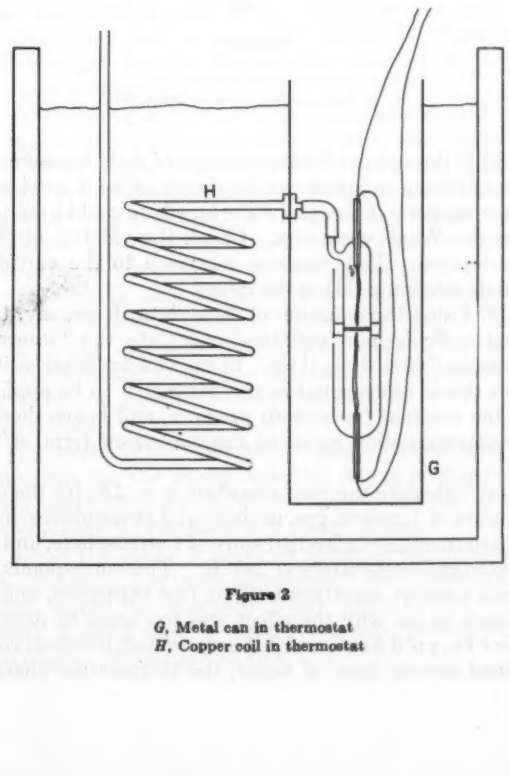


**Figure 2**

*G*, Metal can in thermostat
*H*, Copper coil in thermostat

interest involving $\mu$; in the table are given numerical values for $CO_2$ and $N_2$.

(1) Check the exact thermodynamic relation,[3] $\mu C_p = T\,(\partial V/\partial T)_p - V$, by using good experimental values for $C_p$ (see the table (II)) and by calculating the other quantities from the Beattie-Bridgeman equation of state (*2*). The slight discrepancy in the table must imply inadequate experimental values or (as probably in this case) the slight inadequacy of the empirical equation of state. ($V$ stands for volume per mole.)

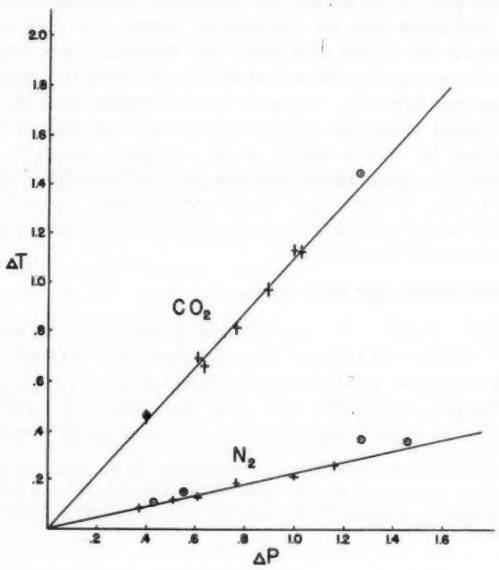


**Figure 3**

+ = points obtained by students
⊙ = Joule and Thomson's original data

(2) If the van der Waals equation of state is assumed, the following equation can be shown to be a good approximation: $\mu C_p = (2a/RT - b)$, where $a$ and $b$ are the van der Waals constants. Check the validity of this assumption. This equation relates $\mu$ to the van der Waals constants (III in the table).

(3) Using the equation of state data (from, say, the Beattie-Bridgeman equation) calculate the "internal pressure," $(\partial E/\partial V)_T$ (IV). In the van der Waals equation this is represented as the correction to be applied to the external (measured) pressure, and hence should be approximately equal to the correction term, $a/V^2$ (V).

(4) Calculate the heat absorbed, $q = \Delta E$, for the expansion of 1 mole of gas, initially at 2 atmospheres, into a vacuum to give a final pressure of 1 atmosphere, and at a constant temperature of 298°K. This corresponds to Joule's earlier experiment (*9*) on free expansion, and it is easy to see why the effect was too small to detect. For $CO_2$, $q$ is 6.5 cal., and if the water bath involved contained several liters of water, the temperature change

**Numerical Data for $CO_2$ and $N_2$[a]**

| *Equation of state data* | $CO_2$ | $N_2$ |
|---|---|---|
| Coefficients of Beattie-Bridgeman equation (*2*) | | |
| $\beta$ | −3.0598 | −0.1497 |
| $\gamma$ | +0.35706 | +0.03518 |
| $\delta$ | +0.00466 | −0.00004 |
| $V_i$ (ideal volume = $RT/P$) | 24.4539 | 24.4539 |
| Calculated from B.-B. equation | | |
| $V$ (actual) | 24.3290 | 24.4478 |
| $(\partial V/\partial T)_P$ | +0.08290 | +0.08225 |
| $(\partial(PV)/\partial P)_T$ | −0.1247 | −0.0061 |
| Coefficients of van der Waals equation (*2*) | | |
| $a$ | +3.61 | +1.31 |
| $b$ | +0.0428 | +0.0373 |
| Heat capacity data (*8*) | | |
| $C_p$ | +0.366 | +0.287 |
| $C_v$ | +0.285 | +0.205 |
| Joule-Thomson coefficients (*2, 3*) | +1.068 | +0.222 |
| Derived quantities | | |
| I $C_{p\mu}$ (experimental) | +0.392 | +0.064 |
| II $C_{p\mu}$ (calculated from B.-B. equation) | +0.375 | +0.063 |
| III $C_{p\mu}$ (calculated from v.d.W. equation) | +0.252 | +0.069 |
| IV $(\partial E/\partial V)_T$ ("internal pressure") | +0.011 | +0.0024 |
| V $a/V^2$ (van der Waals correction term) | +0.0061 | +0.0022 |
| VI $(\partial E/\partial P)_T$ | −0.268 | −0.060 |
| VII $(\partial T/\partial P)_E$ | −0.95 | −0.29 |
| Change in energy for various processes (kg.-cal./mole) | | |
| VIII Increasing average intermolecular distance from 27 Å. (at 2 atm.) to 34 Å. (at 1 atm.) | +0.0065 | +0.0015 |
| IX Evaporation of condensed phase (av. intermolecular distance = 4 Å.) at 1 atm. equilibrium pressure (*2*) | +5.6 | +1.2 |
| X Breaking one chemical bond (av. for $CO_2$) (dissociation to ground states of atoms) (*10*) | +163 | +85 |

[a] $P$ = 1 atm., $T$ = 298°K. Unless otherwise noted, the units are liters, atmospheres, moles, degrees K.

to be observed would be of the order of 0.001°. Note, also, that $q$ provides us with a quantitative measure of the average force between the molecules under normal conditions; for $q$ represents the increase in potential energy (per Avogadro's number of molecules) when the average distance of separation of the molecules is increased by 7 Å. (from 27 Å. at 2 atm. to 34 Å. at 1 atm.) (VIII). This quantity may be compared with similar values for evaporation of the condensed phase (IX), and breaking a chemical bond (X). It is of interest also to calculate the change in temperature of the gas if the free expansion from 2 to 1 atm. is carried out (in our imaginations) under conditions where the gas is thermally isolated, *i. e.*, exchanges no heat with the container (VII).

For the examples chosen, the table provides a quantitative expression of the fact that $CO_2$ deviates much more than $N_2$ from ideality. We feel that carrying out the experimental measurement of the Joule-Thomson

coefficient and performing some of the suggested calculations make more tangible, and give more concrete significance to, the physical picture of a real gas.

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# UNUSUAL BEHAVIOR OF LIQUIDS, RESULTING FROM EXPOSURE TO POLYETHYLENE


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Polyethylene, a high molecular weight polymer, is a widely used plastic. Because of its chemical inertness, it has been recently employed in the form of containers for storage of chemicals such as mercury and inorganic acids. In connection with this application, several unusual effects have been observed.

(1) After using mercury stored in polyethylene flasks for polarographic experiments, it was found that the polarographic maxima of $O_2$, $Pb^{++}$, and $Ni^{++}$ in 0.1 *M* KCl supporting electrolyte were considerably suppressed. A very small decrease of the diffusion current was associated with the suppression of the maxima. Similar effects were observed by storing the 0.1 *M* KCl supporting electrolyte in polyethylene flasks for about 15 hours and using mercury stored in ceramic containers. With this mercury the polarographic maxima are easily obtained under normal conditions. It appears probable that surface-active constituents present in polyethylene are either mechanically removed or dissolved by mercury or the supporting electrolyte. They are possibly responsible for the suppression of the polarographic maxima.

(2) It was found that the dissolution rate of SAE 1020 steel in dilute HCl and $H_2SO_4$ is decreased in the presence of polyethylene. This is consistent with the concept that polarization phenomena involved in the suppression of polarographic maxima resemble the polarization phenomena associated with corrosion inhibition in general.[1]

In 10 per cent air-saturated HCl at room temperature the dissolution rate of steel was decreased by 40 to 60 per cent in the presence of fabricated (polyethylene flasks) or unfabricated polyethylene. The largest decrease of the dissolution rate (around 60 per cent) was observed in cases where the acid was in contact with polyethylene for various periods of time up to several months, prior to testing. The major portion of this effect was observed after only a few days of contact prior to testing. The acid in contact with the polyethylene was either dilute (10 per cent) or concentrated and subsequently diluted to 10 per cent for testing. Similar effects were observed with non-aerated 10 per cent HCl.

In 10 per cent $H_2SO_4$—both air-saturated and non-aerated—the dissolution rate of steel was decreased by 25 to 50 per cent. The lower values of rate decrease were observed in cases where the acid was in contact with polyethylene for several months. This suggests a slow reaction between the active constituents in the polyethylene and sulfuric acid.

The testing time for steel dissolution, for both HCl and $H_2SO_4$, was 16 hours.

(3) The corrosion rate of 1020 steel in tap water at room temperature was decreased by about 30 per cent in the presence of polyethylene in tests of 25 days' duration.

The solubility of the polyethylene constituents responsible for the above reported effects is apparently very small since polyethylene flasks in use for as long as one year did not show any visual change.

From the above it becomes apparent that although the chemical inertness of polyethylene is remarkable, care should be exercised when polyethylene equipment is being used in connection with polarographic and metal dissolution studies.

[1] Gatos, H. C., *J. Electrochem. Soc.*, in press.

# THE GMELIN CHEMICAL DYNASTY

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*(Translated by Ralph E. Oesper)*

HEIDELBERG and Tübingen—two old German university towns on the Neckar—are both well known in America and are often mentioned in chemical circles. Ira Remsen (1846–1927) was at Tübingen during his five-year period of study in Germany (1867–72),[1] and while there as assistant to Rudolf Fittig became the friend and tutor of William Ramsay (the future discoverer of the noble gases). The memory of Remsen's stay remains alive in the University of Tübingen, since the Remsen-Reihlen "Einleitung in das Studium der Chemie" (15th ed., 1950) is still used in the beginning course. Is it necessary to do more than mention Heidelberg and its great chemists Bunsen and Victor Meyer? Göttingen, the third university town of interest here, was graced for many years by the teaching of Friedrich Wöhler (1800–82). Americans trained under him returned to organize the laboratory instruction at Harvard, Yale, and Johns Hopkins.[1]

During the period approximately 1700–1860, these three university cities were the academic sites of the labors of numerous members of the Gmelin family, namely, about a dozen professors of jurisprudence and the sciences, of medicine and chemistry. As in the former ruling houses, or dynasties, it was customary here likewise to distinguish between an older and a younger Tübingen line, and one spoke of three kinds of Gmelin professors: those who had passed away, those who were on the lecture platform, and those who were still in the cradle.

For the chemical historian this dynasty of professors presents the following seven representatives. In genealogical-chronological order they were:[2]

(1) Johann Georg Gmelin (1674–1728), the progenitor of both Tübingen lines. His sons:

(2) Johann Georg Gmelin, Jr. (1709–55) and

(3) Philipp Friedrich Gmelin (1721–68). Their oldest brother Johann Konrad (1707–59) took over the patrimonial pharmacy. His ninth child (among 15) was

(4) Samuel Gottlieb Gmelin (1744–74), scientist. His brother was the apothecary Christian Gottlob Gmelin (1749–1809). One of the latter's seven children was

(5) Christian Gottlob Gmelin (1792–1860), chemist. On the other hand, the five children of P. F. Gmelin (see 3) included

(6) Johann Friedrich Gmelin (1748–1804), scientist, whose youngest son was

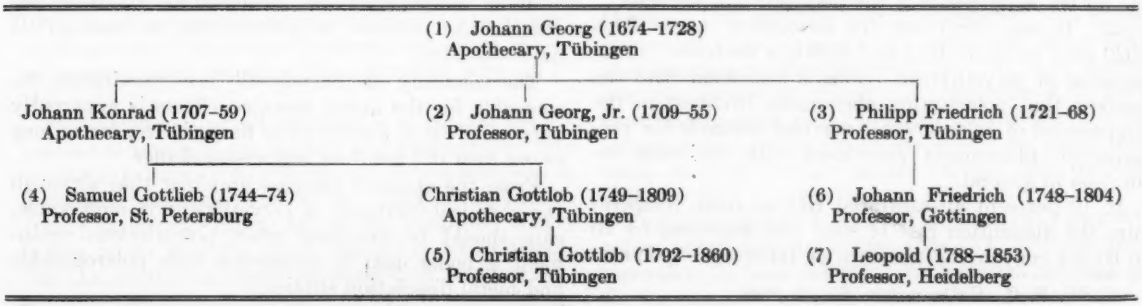
(7) Leopold Gmelin (1788–1853), chemist.

A study of this rare continuity in the choice and creative prosecution of a specific area of knowledge is of significance to the history of chemistry and culture, and likewise to the workings of tradition. This examination also yields valuable insights into the academic surroundings, the course of education, the accomplishments, and personal fortunes of these scientists.

(1) In 1674 a son, Johann Georg, was born to Samuel Gmelin, schoolmaster in Münchingen, a little town in the Duchy of Württemberg, which had suffered greatly from the Thirty Years' War. At the age of 13, the boy began his apprenticeship at Stuttgart, and at 19 as "journeyman" he began his *Wanderschaft* in Ulm, Dresden, Leipzig, Delft (1697) and finally in the Royal "Laboratori chymici" in Stockholm (1699). After seven years he returned home (1706) and through marriage with the daughter of a druggist became the proprietor of an apothecary's shop in Tübingen.

[1] GETMAN, F. H., "The Life of Ira Remsen," Chemical Education Publ. Co., Easton, Pa., **1940**, pp. 31–5. See also VAN KLOOSTER, H. S., *Chymia*, **2**, 10, 13–15 (1949).

[2] Compare "Stammbaum der Familie Gmelin," lxviii + 133 pages and genealogical tables, Karlsruhe, **1877**.



(The building still houses a drug store!) He also held lectures on chemistry from time to time, and enjoyed quite a reputation in the academic circles. His health began to deteriorate in his early fifties; in 1726 he had fainting spells, and a stroke, and after a "burning fever" he died prematurely in 1728.

(2) Johann Georg Gmelin, Jr.,[3] was born at Tübingen in 1709 and died there in 1755. He was the second of the twelve children of J. G. Gmelin, Sr., just discussed. A precocious boy, he was not subjected to the usual apothecary apprenticeship, but instead—at the age of 14—he was enrolled at the local university. He studied the sciences (particularly botany) and medicine, and held his first disputation in 1725. He graduated in 1727, at 18, as licentiate in medicine; his dissertation dealt with the Teinacher mineral spring. He then started on an "educational tour," whose goal was the distant and strange city of St. Petersburg. Peter the Great had founded an Academy of Sciences there in 1725, and two of Gmelin's teachers had been called from Tübingen, namely, Duvernoy, the zoologist, and Bilfinger, the philosopher and physicist. The latter had urged Gmelin to follow him to St. Petersburg. After the University of Tübingen conferred the M.D. degree on Gmelin in 1728, the Academy granted him a salary, and in 1730 he was given a teaching post. The next year, only 22, he was made professor in ordinary of chemistry and science. He delivered lectures (in Latin) and published several short papers on geology, chemistry, etc. It was scarcely possible for him to carry out a genuine chemical research in his own laboratory. Instead, another vast and novel task was offered to him: the leadership of the geographical expedition (together with the historian Gerhardt Fr. Müller and the astronomer L. de l'Isle de la Croyère) within the "second Kamchatka Expedition" planned by the Empress Anna. This expedition through Siberia extended from July, 1733, to the return to St. Petersburg in February, 1743. It showed off Gmelin's competence as a botanist. Its literary product was the monumental "Flora Sibirica" in four volumes (Volumes 3 and 4 edited by Samuel Gmelin) published at St. Petersburg 1747–69, and also his "Reise durch Sibirien," Parts 1–4 published at Göttingen 1751, 1752. On his return to St. Petersburg Gmelin resumed his former offices. After completing the arrangement of his collections for his book, he, the *first* occidental chemist of the Russian Academy, requested (1747) permission to return to Tübingen.[4] Here he became ordinary professor of medicine, botany, and chemistry, whereby he also turned his attention to laboratory instruction in chemistry. A new laboratory (costing 653 florins) was built in 1753, and courses were given there *every three years*. Naturally, these consisted only of demonstrations and qualitative

Johann Georg Gmelin, Sr. (1674–1728)

examination of drugs and so forth, and did not comprise a series of chemical exercises such as those Liebig created at Giessen in 1825. Like his father, he died too soon; his death in 1755 likewise prematurely closed his chemical career.

It should be noted that the scientific education of those days ordinarily took the following course: An early doctorate was not followed by intensification in a specialty through personal experimental researches and an assistantship; rather, the "promotion" was followed by a "scientific tour" of two to three years' duration; its objective was to gain a knowledge of the outside world and to acquire general culture, combined with the inspection of scientific institutes and technical installations (factories, mines, etc.) in foreign lands.

(3) Philipp Friedrich Gmelin (b. 1721, d. 1768 in Tübingen) was the ninth of 12 children (and the sixth of seven sons) of the apothecary Johann Georg Gmelin (compare (1)). Like his brother (compare (2)) he was sent to the University of Tübingen at an early age (15). In 1742 he defended his medical doctoral thesis, and started a two-year "scientific tour" to Holland, England, and the rest of Germany. After his return (1744) he practiced medicine in Tübingen, but maintained contact with the University by lectures. He obtained an extraordinary professorship of medicine (1750), of anatomy (1751), and following his brother's death (1755) succeeded to the ordinary professorship of botany and chemistry. Each three years he conducted practical courses in the laboratory, as dis-

[3] Compare "Johann Georg Gmelin 1709–1755, der Erforscher Sibiriens," Munich, 1911.

[4] By a strange twist of fate, exactly 200 years later, the writer of this paper (Paul Walden) the *last* west-European chemist of the Imperial Academy, also finally landed in Tübingen.

cussed in (2). He also published a number of short papers, program essays, etc. He too died early, at the age of 47.

(4) Samuel Gottlieb Gmelin (1744–74) also began his medical studies at Tübingen when quite young and received the doctor's diploma at 19. The obligatory "scientific tours" took him through France and Holland. In 1768, though only 24, he received a call as

Johann Georg Gmelin, Jr. (1709–55)

professor of natural history to the Imperial Academy at St. Petersburg. Like his famous uncle, the "Siberian traveler" (compare (2)), he was commanded (1768) by Catherine II (the Great) to make a scientific expedition in the Don region and the Caspian provinces. After five successful years, he was recalled in 1773, but on his way back was captured by the Khan of the Chaitakens. The negotiations concerning his release for a ransom of 30,000 rubles were protracted for months, and in July, 1774, the captive succumbed to dysentery. Against his return to Tübingen, he had been named professor of botany in 1768 and also professor of chemistry in 1772. He published the third and fourth volumes of his uncle's "Flora Sibirica," and his own four-volume work, "Reise durch Russland," appeared at St. Petersburg, 1771–86.

An aura of romanticism and the Viking spirit surrounds these youthful German scientists, botanists, and chemists. They had a longing for the faraway and the unknown. They all moved into a cultural vacuum, and as members of the Academy these "academicians" had no real corresponding possibilities of doing scientific work and no intellectual sounding board. In a historical study of the first chemical academicians in Russia, the writer (1909) referred to them as the "traveler academicians,"[5] since they, as courageous explorers, had first of all to learn at first hand the peoples, customs, natural and mineral treasures of the far-flung Russian provinces.

(5) Christian Gottlob Gmelin (1792–1860) followed the family tradition. After obtaining his M.D. degree at Tübingen (1814) he, together with his cousin Leopold (compare (7)), went to Paris. His desire (like that of Liebig in 1822) was to work in Vauquelin's laboratory, to attend the lectures of Gay-Lussac and Thenard, and also to listen occasionally to the great crystallographer Haüy. (The chemical instruction imparted at Tübingen by Kielmeyer could hardly be called satisfactory; in addition to chemistry, he also lectured on botany, materia medica, anatomy, physi-

[5] Compare the article, "Über die Pflege der Chemie in Russland bis zum Ausgang des XVIII Jahrhunderts," by the author in P. Diergart's "Beiträge aus der Geschichte der Chemie," Leipzig, 1909, pp. 369–77. See also his article (*ibid.*, pp. 533–44) on the eminent physico-chemist Tobias Lowitz (b. 1757, Göttingen; d. 1804, St. Petersburg) as Imperial Court Apothecary and Academician. His assistant was C. G. S. Kirchhoff (b. 1764 at Teterow-Mecklenburg; d. 1833 at St. Petersburg). He discovered (1811) the saccharification of starch, and (1814) the action of diastase. Concerning Lowitz, compare LEICESTER, H. M., J. CHEM. EDUC., **22**, 149 (1945), and *Chymia*, **1**, 47 (1949).

Christian Gottlob Gmelin (1792–1860)

ology, and comparative zoology. There was no provision for laboratory work in chemistry.) However, Gmelin was in Paris only a few months. When Napoleon appeared in the Tuileries in 1815, Gmelin hastily left Paris and went to Berlin in order to work with the great analytical chemist M. H. Klaproth (1743–1817). The venerable master had not done experimental work for a long time, nor had he had any students, and his laboratory had fallen into neglect. Consequently, by the end of 1815, Gmelin was again on the move, this time to Stockholm and Berzelius. Gmelin worked there seven months and learned particularly the analysis of minerals. Also, he and Berzelius made excursions together and gathered rocks. The winter of 1816–17 was spent in England, where Gmelin made the acquaintance of Davy (then busy with the construction of his safety lamp), Wollaston, and others. Here again, visits to English and Scotch industrial and mining districts were a source of much information. On the homeward journey he received the pleasant news of his appointment as ordinary professor of chemistry and pharmacy at Tübingen. Therefore, the 25-year-old M.D. and apothecary-chemist sprang, as it were, from the stagecoach into the professorial chair without any previous accomplishments in chemistry and with no teaching experience. He held this post from December, 1817,[6] until May, 1860. He died suddenly, just a few days after turning over the Chemisches Institut to his successor, Adolf Strecker (1822–71).

As teacher and researcher Gmelin did not have an easy row to hoe. His laboratory in the nonheatable rooms of the old palace kitchen (together with the tiny laboratory budget) exerted no attractions. None the less, he carried out mineral analyses and found new facts. Thus in 1818, when analyzing lithia mica, he discovered the red flame reaction of lithium. Likewise, mineral analysis led him to the discovery of ultramarine or artificial lapis lazuli. From 1822 he had been studying the mineral ittnerite, which occurs at Kaiserstuhl (Baden). The ash-gray to bluish-gray mineral turned a beautiful blue when heated; the search for a tinctorial metal oxide was fruitless, and the analysis revealed the presence only of silica, alumina, soda, and sulfate or sulfur. Here was a chemical mystery, and its significance was increased when it was remembered that the costly lapis lazuli, which once was worth its weight in gold, had a similar chemical composition and likewise evolved hydrogen sulfide when treated with sulfuric acid. Could this local mineral be a chemical brother of the precious azure stone imported from China and Hindukush, and might it be made artificially from cheap raw materials? The attempts with insufficient means and the lack of genuine comparison material were greatly handicapped. When Gmelin made his second visit to Paris (1827) he discussed the matter with his former teacher, Gay-Lussac. The result, however, was surprising: in February, 1828, Gay-Lussac reported to the Académie des Sciences that the chemist Guimet had succeeded in preparing artificial ultramarine by a secret process (from the year 1826). Germany at that time had no patent protection for discoveries and inventions, and so in 1828 C. G. Gmelin had to content himself with announcing his findings and to being a sorrowful witness of the speedy installation of the manufacture of ultramarine. His services gained the praise of Liebig, who in his "Chemische Briefe" (1844) stated: "The crown of all discoveries of mineral chemistry with respect to the production of minerals was indubitably the artificial manufacture of lapis lazuli."[7]

Gmelin studied several other minerals, and later investigated some organic natural materials, *e. g.*, the bark of the mezereon (*Daphne mezereum*). He also made physiological studies on the action of rare elements on the animal organism.

In 1837, he wrote a two-volume introduction to chemistry which had original features. Worthy of special note are his services as a pupil of Berzelius, since he translated the first three years (1822–24) of the Swedish master's *Jahresberichte* into German and arranged for their publication in Tübingen. The university there owes to him the erection of a separate, modern chemical building (1846), in which his successors, A. Strecker (to 1869), R. Fittig (to 1876) and then Lothar Meyer[8] carried on. Gmelin's lectures on chemistry were clear and original. He was a friend of the poets Gustav Schwab and Ludwig Uhland.

Even though Gmelin did not found a school, he had one pupil who took the place of an entire school. This was no other than the renowned Julius Robert Mayer

[6] His inaugural lecture was entitled "Historia theoriae combustionis." Moreover, his ancestor Johann Georg Gmelin had published in 1730 a paper with the title, "De augmento ponderis quod capiunt quaedam corpora, cum igne calcinantur." Contemporaneously with Christ. Gottlob Gmelin, there taught at Tübingen his older brother Ferdinand (1782–1848) as professor of medicine and sciences, and Christian Gmelin (1750–1823), son of the above-mentioned Joh. Georg, as professor of law. Regarding the biography of C. G. Gmelin, compare also A. WANKMÜLLER, *Pharm. Zentralbl.*, **89**, 8–12 (1950).

[7] From the standpoint of the history of civilization, the synthesis of ultramarine represents a striking dramatic action, namely, the chemical dethronement or "democratization" of a natural material that at one time was far beyond the reach of the common people. It has been found in the archeological discoveries coming from the royal palace of the Sumerian capital Ur (fourth millenium B.C.), where the excavations have yielded consummately artistic gold jewelry along with mosaic ornaments consisting of mother-of-pearl figures on lapis lazuli backgrounds. Egyptian hieroglyphics reveal that in the second millenium B.C. the nobles of Assu brought the Pharaohs lapis lazuli as tributary offerings. Moreover, as should be noted, a so-called "Babel lazulite" was offered as tribute in addition to the genuine lapis lazuli or bluestone, and the Egyptians themselves manufactured this artificial lazulite. Several Munich chemists (Prandtl, Büchner, and Bertram) analyzed (1926) a specimen of this highly prized bluestone from Babel and found it to be a soda-potash-lime-lead glass colored blue with cobalt and copper. Today the modern ultramarine serves as a cheap oil and water color, used by the laundress and youngest water color artist; it serves to whiten (or blue) paper, linen, starch, sugar, etc. In reviewing the history of this "king of the mineral substances" one may fittingly write: *Sic transit gloria mundi.*

[8] WINDERLICH, R., J. CHEM. EDUC., **27**, 365–8 (1950).

(1814–78), the discoverer (1842) of the "law of conservation of energy."[9] He was a medical student under Gmelin and took his M.D. in 1838 with a dissertation, "Das Santonin." When Berzelius spent a week in the midsummer of 1819 as guest of Gmelin, he was especially struck by the "studied barbaric appearance" of the Tübingen students, who sought to recall the spirit of the days of yore.[10] This somewhat crude custom may perhaps also have been extended to our subject, at least so far as can be deduced from his nicknames: "schwefelsaurer Christian, Schmiedsknecht, Holzspälter."

Of Gmelin's nine children, including three sons, none took over the paternal family apothecary's shop. It was sold in 1844. This step marked the farewell from the good genius of the original firm in Tübingen, a renunciation of pharmacy as a stepping stone to academic posts, a breach in the family tradition. There still remains the venerable original firm, which as formerly is even now known as the "Gmelin Apotheke"; a tablet placed on the house by the University of Tübingen in 1927, on the occasion of the 450th anniversary of its founding, states:

Stammhaus der Tübinger Familie *Gmelin*, zum Gedächtnis ihres Begründers, des Apothekers Johann Georg Gmelin 1674–1728 und der vielen hervorragenden Glieder dieser schwäbischen Familie, insbesondere ihrer zahlreichen Tübinger Hochschullehrer.

This memory is also kept alive by the existence of the Gmelinstrasse in the Tübingen university quarter.

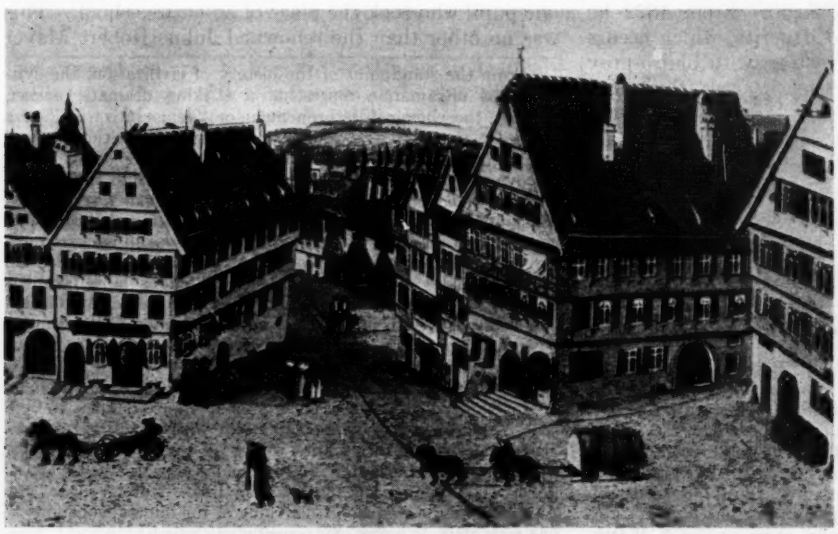
(6) Johann Friedrich Gmelin (b. 1748 at Tübingen, d. 1804 at Göttingen) was the oldest child of Philipp Friedrich (compare (3)). He obtained his medical education at Tübingen and was awarded the M.D. degree at 21 (1769). His "scientific tour" took him to Holland, England, and then Vienna. Returning home (1771) he lectured at the University on natural history and botany; he became (1772) extraordinary professor of medicine at Tübingen. The next year, though only 25, he was called to Göttingen as ordinary professor of philosophy and extraordinary professor of medicine. In 1778 he became ordinary professor of chemistry and botany, and also mineralogy. He was responsible for the erection (1783) of a student chemical laboratory in Göttingen, though it remained for his successor, Fr. Stromeyer (1775–1835)[11] (1805–35) to fit up this building and to initiate a corresponding course of instruction. Gmelin's chemical studies were confined entirely to the qualitative observations usual at that period.

His literary output was important. It included the following books: "Allgemeine Geschichte der Pflanzengifte" (1777); "Einleitung in die Chemie" (1780); "Einleitung in die Pharmazie" (1781); "Chemische Grundzüge der Gewerbkunde" (1795); and particularly the three-volume "Geschichte der Chemie" (1797–99). This latter work was the first attempt to present an extended discussion of the history of the development of chemistry. Of permanent value are the careful compilations of the contents of the writings of earlier authors, but in contrast are the incorrect evaluations of the work of the "ancients," *e. g.*, the dubbing of Paracelsus as a "gold cook," "quack," "charlatan," etc., and Glauber as the "Paracelsus of the seventeenth century."

(7) Leopold Gmelin[12] (b. 1788 at Göttingen, d. 1853 at Heidelberg) was the youngest son of J. F. Gmelin (compare (6)). After finishing the course at the lyceum at Göttingen, he, at 16, attended his father's lectures on mineralogy. In 1804 he was sent to Tübingen to work in the family apothecary's shop, and (also traditionally) to study at the university there. He pursued the courses in medicine and mathematics; from 1805 to 1809 he was at Göttingen for medicine and chemistry (under Stromeyer). He took his medical degree at Göttingen in 1812; the dissertation was

[9] OESPER, R., J. CHEM. EDUC., **19**, 134 (1942).

[10] BERZELIUS, J. J., "Reiseerinnungen aus Deutschland," Verlag Chemie, **1948**, p. 2 ff. See also OESPER, R., J. CHEM. EDUC., **26**, 202 (1949).



Gmelin Apotheke in Tübingen: Corner House on Left

[11] Stromeyer discovered cadmium in 1817. His most distinguished student was Robert Bunsen (1828–31) and his eminent successor (1836) in the chair at Göttingen was Friedrich Wöhler (1800–82). Compare J. CHEM. EDUC., **30**, 202 (1953).

[12] Compare PIETSCH, E., *Ber.*, **72A**, 5 (1939), and also the papers issued by Pietsch in 1938 to commemorate the 150th anniversary of Gmelin's birth.

based on an experimental study he had made in Vienna on "The black pigment of steers' and calves' eyes." After a stay in Italy (1812–13) he carried out an analytical investigation under Stromeyer's guidance on the mineral haüynite (1813) and habilitated with this study at Heidelberg in the fall of 1813. The very next year he was advanced to extraordinary professor. In 1814–15 he and his cousin Christian Gottlob (compare (5)) made a study trip to Paris. In 1817, he was promoted to ordinary professor of chemistry (and medicine, as he signed himself) in the medical faculty at Heidelberg. His three-volume "Handbuch der theoretischen Chemie" appeared in 1817–19. Altogether, very busy and fruitful years. The family motto, *Festina lente*, would have seemed to advocate a less hectic pace.

Gmelin turned gray early; by his fifth decade he was snow-white "like a blooming cherry tree."

He lectured on inorganic and organic chemistry, analytical chemistry, metallurgy (with excursions), and materia medica. His delivery was often hesitant and punctuated with sudden interruptions. The first stroke in the spring of 1848 was followed by others, and in 1851 he asked for retirement. This success-filled life came to an end on April 4, 1853.

Gmelin's experimental activities fell principally in the years (1815) 1820–47.[13] He put out about 28 papers on mineralogical-inorganic topics, and 20 of physiological-organic nature. Of greater scientific interest are the later (after 1820) papers, in which he had the collaboration of Friedrich Tiedemann (1781–1861), professor of anatomy and physiology at Heidelberg. They made a physiological-chemical study of digestion (1820–26), the gall and blood; and in the course of their work they isolated, for the first time, taurin (in ox-gall, 1824), cholic acid, hematin (in blood), pancreatin (1826), and they discovered that saliva contains potassium thiocyanate. In the mineralogical-inorganic field, the important points were: the study of lapis lazuli (1815, compare (5)); the conversion of yellow prussiate of potash into the red salt (1822) (the latter compound is his discovery); the discovery of the mysterious croconic acid on the reduction of $K_2CO_3$ by carbon (1825).

Leopold Gmelin's fame rests primarily on his great literary feat, his "Handbuch der theoretischen Chemie." It appeared first (1817) in three thin volumes, and in successive editions, issued to the year of his death, grew into a multi-volume reference work. It is the product of an exemplary concentration of effort on this simple problem: To arrange systematically all the precisely determined facts concerning every element and compound, to state these facts succinctly and accurately, and also to give the pertinent references to the literature. In this task he proceeded logically in a calm and critically inquiring manner, regarding every

[13] The period 1816–19 shows a definite pause in his experimental studies. He was occupied with preparations for his lectures and the composition of the first edition of his "Handbuch" (1817–19).

Johann Friedrich Gmelin (1748–1804)

speculation as hazardous. "Nothing was in keeping with the times except the temperate consideration of observations, and Gmelin was the right man to represent a tendency of this kind. He united boundless industry with wide knowledge and he understood how to turn both of these qualities to account in his *Handbook*. In adducing facts, completeness and conscientiousness were his watchwords, and these were adhered to."[14] From the first edition on, and for the first time in German textbooks, he employed the conceptual formulation "organic chemistry"; he speaks of the "imponderable elements" (heat, light, electricity) and devotes considerable space to them along with the "ponderable elements." He also coined new terms, *e. g.*, "Traubensäure" in place of "Vogesensäure," "Ester" instead of "Saureäther," "ketones" as a class name. He used the Laurent "Nucleus Theory" as the basis for the systematization of the organic compounds, and gives names to the "nuclei" (*radicaux*). His "Handbuch der Chemie" was *the* book of chemistry for more than a generation, and it exerted a fundamental influence on the development of the science, not only through its character as a canon of facts, but also because of the theoretical views presented in it. However, the latter proved to be a disturbing and retarding influence on the development of the atomic views, particularly of the Berzelian system of atomic weights. Contrary to

[14] LADENBURG, A., "History of Chemistry," translated by L. DOBBIN, Edinburgh, 1900, p. 174.

the latter, Gmelin and his school advocated the theory of the stoichiometrically determinable combining weights or equivalents[15] such as H = 1, O = 8, C = 6, S = 16, water = HO, etc. The chemical valence of the elements did not enter as the prime factor, and the atomic and molecular theories were regarded as incidental. The confusion in the chemical literature with respect to the ideas of atom-equivalent and molecule increased to such an extent that the editor of the *Journal für praktische Chemie* (Erdmann in Leipzig) wrote: "Every paper must be preceded by a key as in music." The resolution of this critical state was the objective of the famous convention (the first international chemical congress) which met at Karlsruhe (Baden) in September, 1860, at the invitation of Kekulé, Wurtz, and Weltzien.[16] All this might be set down as a black mark against Gmelin when one is considering the lasting values of his career.[17]

One of Gmelin's great services was his persuading the young Wöhler to turn to chemistry. He induced the 23-year-old medical doctor to study chemistry with Berzelius at Stockholm (compare (5)) and thus nipped in the bud Wöhler's intention to become a practicing obstetrician.[18]

In 1922 the Deutsche Chemische Gesellschaft assumed the continuation of the monumental "Handbuch der anorganischen Chemie" (eighth edition). The work (which from the fifth edition on had not been supervised by Gmelin himself) had to be fundamentally revamped both internally and externally. The name "Gmelin" was retained as a symbol of the scientific purpose of the new work. Since 1935 the editorial board has been under the direction of Erich Pietsch.[19] The activities are now centered at Clausthal, the Gmelin Institut, which was created by Pietsch, whose energy and initiative successfully made possible the move from Berlin after the Hofmann Haus was destroyed. He mobilized the material assistance of the ERP, which is thus furnishing another instance of the cooperation of the U. S. A. for the rebuilding of Germany, and under the sign of the old "Gmelin" there has emerged a new spiritual bond between our two cultures.

These "brief biographies" have presented data of interest not only regarding the history of chemistry and chemical personalities but also applying to general and university history. The first point of interest is the fact that all of these chemists went through the medical course of study and came to chemistry with the M.D. degree and uniformly at a young age (18–21 years). Secondly, to us moderns it seems strange that these doctors immediately went on "tours" instead of going into the laboratory to deepen their chemical knowledge by research. Thirdly, these journeys, usually of about two years' duration, seemed to be adequate qualifications for appointment for a chemical chair. It is a fair question: when and where was the chemical education obtained? Or, in those days was there really a chemical curriculum and was laboratory instruction actually available?

The science which Paracelsus[20] had once established through a revolutionary overturning of academic tradition had persisted as iatrochemistry through three centuries, and as late as 1840 Liebig[21] wrote concerning the recent past: "Chemistry was the handmaiden of the physician, for whom she prepared purgatives and emetics; ingrafted in the medical faculties she could not attain independence. Only the medical student learned to know her of necessity; except for him and the pharmacy student she did not exist."

Consequently, at the beginning of the nineteenth century there still persisted this spiritual and practical dependence of chemistry on medicine in the Paracelsian sense. This fact refutes[22] the view that Robert Boyle endowed chemistry with new goals and fundamentals, and that he was the "founder of modern chemistry."[23] The crucial point was the separation of chemistry from medicine—in spirit and doctrine—by the removal of chemistry from the medical faculty and its inclusion in the philosophical faculty as an independent discipline. The first to take this anti-Paracelsian step was the Weimarian minister, poet, and scientist J. W. Goethe[24] who, in 1789, without the consent of the University of Jena, appointed the apothecary J. F. Göttling (1753–1809) as professor of chemistry in the philosophical faculty and designated as his successor (from 1810) the gifted J. W. Döbereiner (1780–1849).[25] And did not the 21-year old Liebig go (1824) from Gay-Lussac's private laboratory in Paris directly to a professorship in the philosophical faculty at Giessen, by appointment and not by election?[26] Only then was the way indicated and made free for chemistry to live a scientific life of its own, and also for the second cardinal question: instruction in a chemistry laboratory. Gradually the viewpoint prevailed that old, poorly heated "palace kitchens" (as in Tübingen and Jena) were *not* still good enough for chemistry, and that secularized monastic buildings with scanty facilities and maintenance funds—despite the monkish admonition: *ora et labora*—were not fit places for chemical instruction and research (as had been the case in Heidelberg and Breslau, for instance).

Hence, in spite of the limitations imposed on them, the Gmelins, as teachers and augmenters of chemical

[15] VON MEYER, E., "History of Chemistry," translated by G. McGowan, New York, 1906, pp. 237, 302, 306.

[16] DEMILT, C., *Chymia*, 1, 153–69 (1948).

[17] It must, however, be pointed out that according to the preface in the 4th edition of the "Handbuch" (since 1843) Gmelin "definitely has gone over to the atomic hypothesis."

[18] In a sense, Wöhler did realize his youthful intentions, since as the great synthesist he officiated at the "birth" of many new chemical "individuals."

[19] OESPER, R., J. CHEM. EDUC., 26, 251 (1949).

[20] PARACELSUS, "Paragranum," 1530.

[21] LIEBIG, J., *Ann.*, 34, 102 (1840).

[22] WALDEN, P., *Naturwissenschaften*, 37, 169–72 (1950); compare also SARTON, G., *Chymia*, 3, 163, 189 (1950).

[23] PARTINGTON, J., "A Short History of Chemistry," London, 1937, p. 67.

[24] WALDEN, P., *Naturw. Rundschau*, 2, 536–43 (1949).

[25] PRANDTL, W., J. CHEM. EDUC., 27, 175 (1950).

[26] OESPER, R., J. CHEM. EDUC., 4, 1461 (1927).

facts, worked unswervingly as pioneers in the movement for the establishment of an independent science of chemistry, actuated directly by the impressions they had gained on their educational journeys. From first to last, they were conscious of the honorable and responsible tradition of the name *Gmelin*.

# LABORATORY ADHESIVES

**MAXEY BROOKE**
Phillips Petroleum Company, Sweeny, Texas

Ask the average chemist what adhesives he uses in the laboratory and he will probably look at you blankly. Insist that he tell you and he might answer, "Well, there is deKhotinsky, of course. And label cement. Let's see, rubber and plastic cement, and glue and paste. I sometimes use litharge and glycerine. Oh yes, glass wax and solder." And the list goes on and on, usually to the surprise of our chemist, who didn't realize the wide variety of materials which he must join at one time or another.

The most of these cements, pastes, mucilages, glues, solders, and waxes are bought ready-prepared. But on occasion the chemist must make his own. In any event, it is a source of satisfaction to know the composition of the materials used, and their preparation makes excellent student projects.

DeKhotinsky cement is synonymous with laboratory cement. Many formulas of varying complexity have been proposed. In essence it is simply a tempered shellac, and a simple formula is 70 parts orange shellac and 30 parts pine tar melted together and cast into sticks. A harder cement can be made by increasing the shellac and a softer one by increasing the tar.

Many cements are made by simply dissolving the material to be cemented in a volatile solvent. Rubber cement is prepared by dissolving pure gum rubber in benzene to make a thick liquid. Plastic cement is made by dissolving celluloid, pyroloxyn, cellulose acetate, etc., in acetone. Old tooth-brush handles are especially good raw materials.

Bottles need labels and labels need glue. A formula for label cement said to be noncurling is:

| | |
|---|---|
| Casein | 100 parts |
| Powered mica | 100 parts |
| Boiling water | 850 parts |
| Borax | 25 parts |
| Sodium fluoride | 25 parts |
| Pine oil | 6 parts |

For those who like old-fashioned starch paste, the following is a popular book-binders' recipe. Mix 1/2 cup of flour and 1/2 ounce of alum. Add water to form a thin paste. Add 2 cups of water and boil five minutes. Three or four drops oil of cloves improves the keeping quality. Make up weekly.

Soft or semisoft waxes find wide application in the laboratory. Pellerano (*10*) proposes the following nonhardening wax for glass-to-glass seals.

| | |
|---|---|
| Tallow | 340 parts |
| Mineral oil | 50–100 parts |
| Aluminum oleate | 50–100 parts |
| Rosin oil | 50–100 parts |
| Powdered soapstone | 400–1000 parts |

For sealing brass to glass, several cements are used (*4*), for example:

Faraday's cement: 5 parts rosin, 1 part beeswax, 1 part red ocher.

Singer's cement: 20 parts rosin, 4 parts beeswax, 4 parts red ocher, 1 part plaster of Paris.

Varley's cement: 16 parts black rosin, 16 parts dry whiting, 1 part beeswax.

In all three formulas the ingredients are melted together and cast into convenient form.

A putty said to be resistant to hydrochloric acid is composed of:

| | |
|---|---|
| China clay | 54% |
| Dehydrated tar | 38 |
| Anthracene oil | 2.7 |
| Asbestos wool | 5.3 |

Jackson (*7*) has proposed a general laboratory cement for gas-tight joints:

| | |
|---|---|
| Asphalt | 1 part |
| Rosin | 6 parts |
| Rubber | 3 parts |
| Turpentine | 1 part |

The rubber is dissolved in the melted asphalt and rosin and held at just melting temperature for 2–3 hours. The turpentine is added and the mixture is cast into sticks.

The next group of adhesives are specific for joining materials to themselves:

*Porcelain to porcelain:*

| | |
|---|---|
| White shellac | 50 parts |
| Mastic gum | 35 parts |
| Venetian turpentine | 10 parts |
| Zinc oxide | 5 parts |

Melt together and apply hot.

*Cellophane to cellophane (6):*

| | |
|---|---|
| Gum arabic | 16.5 g. |
| Glycerine | 29.5 g. |
| Water | 49.5 g. |
| Formaldehyde (40%) | 4.5 g. |

*Bookbinding adhesive (3):*

| | |
|---|---|
| Glue | 33.30% |
| Sorbitol (83%) | 12.54 |
| Glycerine | 4.16 |
| Water | 50.00 |

*Fireproof glue (4):*

Heat 1 part animal glue and 8 parts raw linseed oil until homogeneous. Stir in 2 parts quicklime.

Cements are a class of adhesives which are plastic when applied but set up hard, either when cast into a form or when used to join materials. Moore (9) has described both an acid- and an alkali-resistant cement which are stable to about 130°F.

*Acid-resistant cement:*

| | |
|---|---|
| Barium sulfate | 3 parts |
| Asbestos | 1 part |
| Sodium silicate | 2 parts |

*Alkali-resistant cement:*

| | |
|---|---|
| Manganese dioxide | 10 parts |
| Iron filings | 40 parts |
| Portland cement | 20 parts |
| Water | 40 parts |

A sulfur cement formula, also acidproof, is furnished by Duecker (5): Melt together:

| | |
|---|---|
| Thiokol | 4 parts |
| Sulfur | 36 parts |
| Sand | 60 parts |

A cement useful for filling cracks in cast iron (Smoothon) is prepared by mixing:

| | |
|---|---|
| Precipitated iron powder | 60 parts |
| Ammonium chloride | 2 parts |
| Sulfur | 1 parts |

Make into a smooth paste with water just before using.

Magnesium oxychloride cement is very useful for joining ceramics to ceramics. It can also be used for casting small articles since it is cold-setting. Bennett (2) gives the formula:

Mix dry:

| | |
|---|---|
| Magnesium oxide | 40 parts |
| Barium sulfate | 40 parts |
| Chalk | 20 parts |

Add to:

| | |
|---|---|
| Magnesium chloride solution, 27°Bé. | 60 parts |
| Hydrochloric acid, 21°Bé. | 20 parts |
| Sulfuric acid, 22°Bé. | 20 parts |

It is frequently necessary to join many materials to metal. No general formula can be used. Several specialized formulas have been suggested:

*Metal to metal (1):*

| | |
|---|---|
| Bleached shellac | 100 parts |
| Sandarac gum | 40 parts |
| Castor oil | 15 parts |
| Denatured alcohol | 430 parts |

*Paper to metal (3):*

| | |
|---|---|
| Wheat starch | 100 parts |
| Water | 700 parts |
| Gelatin | 10 parts |
| Sodium silicate | 100 parts |
| Turpentine | 50 parts |

Mix starch with half the water and the gelatine with the other half. When dissolved, combine and mix in the silicate and turpentine.

*Felt to metal (11):*

| | |
|---|---|
| Sodium silicate | 60 parts |
| Emulsified asphalt | 12 parts |
| Clay | 28 parts |

*Glass to metal (8):*

| | |
|---|---|
| Powdered quartz | 62 parts |
| Sodium silicate | 14 parts |
| Water | 14 parts |
| Aluminum fluoride | 10 parts |

*Glass to metal, metal to metal (6):*

| | |
|---|---|
| Litharge | 260 g. |
| Glycerine | 66 ml. |
| Water | 33 ml. |

Mix thoroughly, apply immediately, and allow to set 24 hours before using. The cement is waterproof and ammonia-resistant.

The final group of adhesives are solders. Soft solder, m. p. 188°C., is composed of lead, 50 per cent, and tin, 50 per cent. It is used with a zinc chloride or rosin flux. Intermediate solder, m. p. 400°C., is composed of silver, 20 per cent; copper, 3 per cent; zinc, 2 per cent; and tin, 75 per cent. The same fluxes are used. Hard solder, m.p. 720°C., is composed of silver, 45 per cent; copper, 30 per cent; and zinc, 25 per cent. It is used with a borax flux.

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# COULOMETRIC TITRATIONS

## *A Laboratory Experiment*

**CHARLES N. REILLEY**
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COULOMETRIC methods of analysis are made possible by Faraday's fundamental researches upon electrochemical equivalence. Quantitative experiments using the coulometric principle have long been included in physical chemistry courses, but only recently has there existed much stimulation for incorporating this principle in analytical determinations.

Electrodepositions based on the works of Claasen, Fischer, Luckow, Land, and Treadwell have been the basis for many analytical separations and determinations but these processes do not rely upon the measurement of the amount of current nor upon operation at 100 per cent current efficiency and therefore are not considered as coulometric procedures.

Coulometric procedures may be divided into two general classes: those carried out at controlled electrode potential and those at constant current.

In the *controlled potential* method, the working electrode is kept at a fixed potential such that only the desired reaction can take place. The current decreases as the process proceeds, so that the total amount of current (coulombs) must be determined by means of an external coulometer (*1, 9, 10, 11*) or by experimentally fitting a mathematical expression for the current-time relationship (*13*). The controlled potential method, though possibly more versatile than the constant current procedure, requires more time and involves the additional step for calculating the total number of coulombs.

*Constant current* procedures require only a knowledge of the constant current and elapsed time to determine the number of coulombs. These procedures have been applied in two ways: electrolytic stripping of plated deposits and coulometric titrations. The stripping of plated deposits has been used to measure the thickness of metal and metal oxide films (*2, 6, 12*) as well as to determine the quantity of the plated metals in chronopotentiometry.

Coulometric titrations (*3, 5, 7, 8, 14*) have been so named because a definite amount of reagent is generated in the solution electrically, this amount being directly determined by the number of coulombs. The equivalence point may be detected in any of the familiar ways (amperometric, potentiometric, photometric, with indicators). Some typical coulometric titrations are summarized in the table. Coulometric titrimetry has several unique advantages:

(1) *No Standard Solutions Required.* In coulometric titrations the primary standard is the *voltage* of the standard cell (employed to determine tne value of the current) and the *frequency* of the alternating current used to operate the timer. Thus this single composite standard can replace a host of different chemical standards employed in the various possible titrations. Standard solutions can be prepared coulometrically by generating the desired chemical in a solution and diluting the resulting reagent to a known volume (*3*). In short, the electron is a most versatile reagent.

(2) *Utilization of Unstable Reagents.* Unstable reagents may be generated and used on the spot so that time for them to decompose or evaporate will be considerably decreased. An excellent example of this is the generation of chlorine (*5*) as a reagent. The preparation, storage, and precise transfer of a standard solution of chlorine by the usual volumetric means would be an extremely difficult task. Yet chlorine may be easily prepared in known quantity by electrolysis of a sodium chloride solution.

(3) *Pretitration of Impurities.* By pretitration of the generating solution before addition of sample,

**Coulometric Titrants**

| *Titrant generated* | *Substance for generation* | *Substance titrated* |
|---|---|---|
| | *Anodic generation* | |
| $H_3O^+$ | $H_2O$ | Bases |
| $Cl_2$ | $Cl^-$ | $As^{+3}$; $SO_3^{--}$ |
| $Br_2$ | $Br^-$ | $As^{+3}$; $Sb^{+3}$; $I^-$, $H_2S$, $SO_2$ $Tl^+$, $UO^{++}$; $Cu^+$ $CNS^-$; $N_2H_4$; $NH_2OH$ Thiodiglycol; mustard gas; 8-hydroxyquinoline; aniline; acrolein, resorcinol, thioether |
| $I_2$ | $I^-$ | $As^{+3}$; $S_2O_3^{--}$ |
| $Ce^{+4}$ | $Ce^{+3}$ | $Fe^{++}$; hydroquinone; aminophenols |
| $Ag^+$ | Ag | $Cl^-$; $Br^-$; $I^-$ |
| | *Cathodic generation* | |
| $OH^-$ | $H_2O$ | Acids |
| $Fe^{++}$ | $Fe^{+3}$ | $MnO_4^-$; $VO_3^-$; $CrO_4^{--}$; $Br_2$; $Cl_2$ |
| $Cu^+$ | $Cu^{++}$ (in $Cl^-$ or $Br^-$ media) | $CrO_4^{--}$; $VO_3^-$; $Br_2$ |
| $Ti^{+3}$ | $Ti^{+4}$ | $Fe^{+3}$ |
| Cu | $CuI_2^-$ | $Fe^{+3}$; $Cu^{++}$ |
| Sn (→ $SnCl_2$) | $Sn^{+4}$ (in $Cl^-$ media) | $Fe^{+3}$ |

much more accurate results can be obtained. Further, since the end-point indicator corrections are automatically cancelled and the effect of impurities in the generating solution is minimized, the method can be applied to solutions of much greater dilution. The importance of this characteristic is too often underemphasized.

(4) *Ease of Micro-addition of Reagent.* Currents of the order of 60 electrons per second can be measured using modern electrometer tubes (*4*). Hence it seems that there is no practical minimum to the magnitude of currents that can be used to generate reagents electrically—the difficulty always lying in the detection of the equivalence points. The amperage of the current (analogous to the strength of a volumetric reagent) can be set accurately to almost any level, and extremely small quantities can easily be added near the equivalence point.

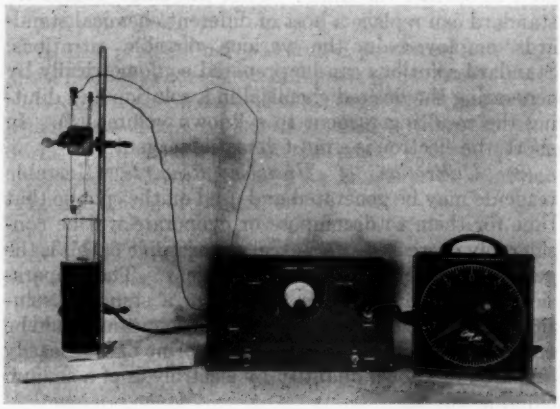

**Figure 1. Complete Coulometric Apparatus**

(5) *No Dilution.* Since the titrant is actually the electrons themselves, addition of titrant does not cause dilution of the sample solution. This is of particular importance in the titration of microgram quantities of materials because dilution can alter the pretitrated reference state of the indicator in such a manner that the procedure described under advantage (3) will no longer be corrective. For this reason the internal generation procedure (*7*) is much preferred over the external generation procedure (*3*) in estimating microgram quantities coulometrically.

(6) *Remote Operation.* Because the amount of titrant added and the detection of the equivalence point may both be electrical in nature, it is relatively simple to operate at more remote distances than would be feasible with regular volumetric procedures. This is of particular significance in titrations of radioactive or dangerous materials.

(7) *Automatic Procedures.* Because of the large amount of research in the development of electronic control circuitry during the past decade, automatic titrimetry is made especially simple when all controlled quantities can be made electrical in nature, as is the case with coulometric titrimetry.

## TITRATION

The principle of coulometric titrimetry has been successfully demonstrated in our instrumental laboratory course, using the instrument shown in Figure 1. In the analysis, students are given liquid samples of the stock arsenite solution accurately measured from a buret. After dilution to exactly 100 ml., 10-ml. aliquots are titrated by electrically generated iodine. Starch is used to indicate the end point. The potassium iodide solution is pretitrated until the first permanent blue-violet color before the first aliquot is added. This blank correction is necessary since a small quantity of arsenite is placed in the KI stock solution to insure that no iodine will be present in the initial solution from air oxidation of iodide. Practice runs may be made with the stock arsenite to check reproducibility of procedure and to standardize the arsenite. With care, students will obtain precision and accuracy within two parts in a thousand.

Although other end-point techniques could be used, the visual end point helps to emphasize that the electrodes in the solution are for *generating* reagent and not for *indicating* an end point. The use of indicator electrodes tends to be especially confusing to students since *potentio*metric, *conducto*metric, and *ampero*metric refer to several different ways of determining an end point whereas *coulo*metric, like *volu*metric, refers to the method of measuring reagent quantity.

The necessary stock solutions consist of 12 g. $As_2O_3$ per 4 liters of solution (slightly acid for stability); a 1 molar solution of $Na_2SO_4$ for use in the separated cathode compartment; and a buffered KI solution (240 g. KI, 41 g. $NaHCO_3$, water sufficient for 4 liters of solution, 1 ml. $As_2O_3$ solution).

## COULOMETRIC CELL

The anode is a 2 × 3-cm. platinum-foil electrode made by fusing a platinum wire into soft-glass tubing and subsequently spot-welding the foil to the wire (heating the wire and foil with a burner and tapping at the same time with a small hammer will accomplish the same result). The cathode must be isolated from the body of the solution so that the electrically generated iodine formed at the anode will not be stirred into direct contact with the cathode and thus be reduced. For this purpose a fine fritted disc filter stick is filled with an inert electrolyte (1 *M* $K_2SO_4$), and a platinum wire is then immersed in this tube for cathodic contact. These two electrodes are immersed in a 150-ml. beaker containing 50 ml. of buffered KI solution. Rapid stirring is accomplished by means of a magnetic stirrer. When the current passes through the cell, the anode reaction is

$$2I^- - 2e \rightarrow I_2$$

and the cathode reaction is

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

The products of the cathode reaction will only slowly diffuse into the solution proper, and will in any case have relatively small effect.

The cathode electrolyte was chosen to be $K_2SO_4$ since acid electrolytes have a tendency to generate hydrogen peroxide from oxygen of air.

## COULOMETRIC SUPPLY

This supply was designed specifically for student use in this particular experiment, but could also be used in other experiments such as the determination of the electrochemical equivalence of silver or in determining transference numbers by the Hittorf method.

To operate (see Figure 2), the power switch, $S_1$, is turned on and the set is allowed to warm up for five minutes. The current (approximately 50 ma.) is standardized versus an internally contained mercury battery (Mallory RM-12 used as a standard cell) by pushing the button in the upper right-hand corner and turning the "calibrate" knob until the meter reads zero. The instrument is now ready for use. When the output switch, $S_2$, is thrown to "on" (down position in Figure 2), the timer commences to operate and simultaneously a constant current flows through the cell. This output switch, therefore, is analogous to the stopcock on a buret. Small additions of reagent can be added by a quick flip of the switch on and off. A convenient time for a titration is around 500 seconds. This time is a compromise between accuracy of timing and boredom to the operator.

The instrument is readily assembled and has required very little attention. In fact, a graduate student with no prior knowledge of electronics duplicated the original model in less than one day.

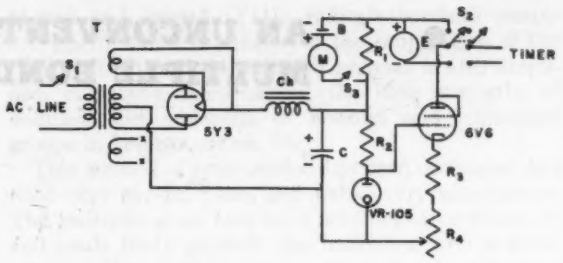


**Figure 2. Schematic Diagram for Constant-current Supply**

*B*, RM-12 Mallory mercury battery (see text). *C*, 10 mfd. 450-v. electrolytic condenser. *Ch*, Stancor C1002 filter choke, 10.5 Hys., 110 ma. *E*, Electrolytic (coulometric) cell (see text). *M*, d.-c. meter, 15-0-15 ma. A more sensitive meter can be used if resistor is placed in series or parallel. $R_1$, 30-ohm, 10-watt wire-wound resistor. $R_2$, 20,000-ohm, 10-watt wire-wound resistor. $R_3$, Resistance value varied but was approximately 2300 ohms and was made by using a 2000-ohm, 25-watt resistor and a smaller resistor (*e. g.*, 300 ohms, 5 watts) in series. $R_4$, 250-ohm, 25-watt variable resistor (Ohmite 0154). $S_1$, SPST toggle switch. $S_2$, DPDT toggle switch. $S_3$, Tap key from war surplus (Mallory 2001 should be suitable replacement). *T*, Stancor PM8409 power transformer (700 VCT, 90 ma., 5-v., 2 a.; 6.3-v., 3 a.). Winding with leads, *zz*, goes to filament (not shown) of 6 V 6. Timer, GraLab Micro-Timer type 202, mfd. by Gray Laboratory and Mfg. Co., Dayton, Ohio. Cabinet, sloping front cabinet from Par-Metal Products, Long Island City, N. Y. (14 × 8 × 8).

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## CORRECTION

The derivation included in our article, "A kinetic interpretation of the Bouguer-Beer law," this Journal, **31**, 417 (1954), is essentially the same as that in an article by F. C. Strong, *Anal. Chem.*, **24**, 338 (1952). We unfortunately overlooked Dr. Strong's article and wish to call attention to his publication.

—*J. H. Goldstein and R. A. Day, Jr.*

# AN UNCONVENTIONAL REPRESENTATION OF MULTIPLE BONDS

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NORMAL practice has always been to write a horizontal stroke between the symbols for two elements to represent the two electrons of a single covalent bond. Following this practice, four-electron bonds are represented by two strokes and six-electron bonds by three. The identity of the strokes tacitly implies the identity of the bonds, although many occasions arise in which this is undesirable. That a double bond is not two single bonds has been appreciated for many years on chemical grounds, and we now have also a physical picture of the difference between the pairs of electrons in a multiple bond.

In order to emphasize the difference in chemical reactivity of the $\sigma$ and $\pi$ electrons in a double bond, the authors have found that a very useful device for teaching purposes is to represent the $\sigma$ electrons by a stroke as usual, but to indicate the $\pi$ electrons by a pair of dots placed above the stroke, thus:

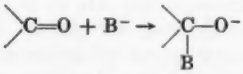
$$X\overset{\cdot\cdot}{=}Y$$

Students immediately appreciate from this picture that there are two electrons available to take part in all of the addition reactions which occur, but that there is still a bond present of the same type as simple single bonds, which form the essential skeleton of molecules and which are not ruptured by most normal reagents. This method of representation has an advantage if one wishes to use the curved arrow to indicate conjugative (tautomeric) effects.

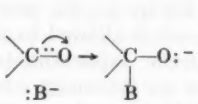
I II III IV

I helps better than II to emphasize that the curved arrow refers to the $\pi$ pair of electrons only; III and IV show the presence of both conjugative and inductive effects with greater clarity than other methods.

The ground is now prepared for a discussion of addition reactions by ionic mechanisms, both electrophilic and nucleophilic, as well as radical additions and polymerizations. To give a concrete example, the familiar question, "Where do the electrons go to?" when the student is faced with the more conventional formulation:



has its answer implicit in the representation:



All of this can be taught without discussing any physical picture of the bonds at all. However, even elementary students have little trouble in appreciating that the $\sigma$ bond has axial symmetry, whereas the electrons in a $\pi$ bond can be considered to move in one plane. They can usually take the further step of visualizing the six-electron bond as having one $\sigma$ type bond and two $\pi$ type electron pairs with their planes perpendicular to one another. This is represented as

$$X\overset{\cdot\cdot}{\underset{\cdot\cdot}{=}}Y$$

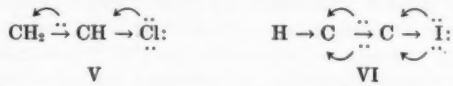
with the convention that placing the dots on opposite sides of the stroke indicates that the planes of the orbitals are at right angles. Extending this, cumulated systems are written

$$X\overset{\cdot\cdot}{=}Y\underset{\cdot\cdot}{=}Z$$

and we can introduce the idea that the XY $\pi$ pair do not interact directly with the YZ $\pi$ pair since neither has a vector component in the other's plane. On the other hand, conjugated systems are represented

$$W\overset{\cdot\cdot}{=}X\text{—}Y\overset{\cdot\cdot}{=}Z$$

to show that the WX and YZ $\pi$ pairs *can* have their planes parallel, and thereupon interact. Indeed, our experience is that the whole idea of delocalization of electrons is best introduced and treated in this way. The electronic interactions in molecules such as vinyl chloride are better appreciated when seen as V, where the fact that only one of the three lone pairs on the chlorine can interact with the double-bond $\pi$ pair is



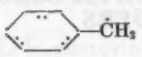
V VI

readily obvious. In iodoacetylene (whose dipole moment is practically zero), VI shows nicely that there are two such similar interactions.

From the concept of delocalization in conjugated aliphatic compounds, it is not a difficult step to a consideration of benzene and other aromatic systems. We have used the convention, with respect to orbitals originating on ring atoms, that dots within the ring represent electrons whose orbitals are perpendicular to the plane of the ring, and dots outside indicate those

with orbitals parallel to its plane. Aromatic substitution can be very effectively discussed against this background, and greater clarity given to such topics as the basicity of heterocycles, and the reactivity of the phenyl radical, VII. Without graphic assistance, stu-

VII




VIII

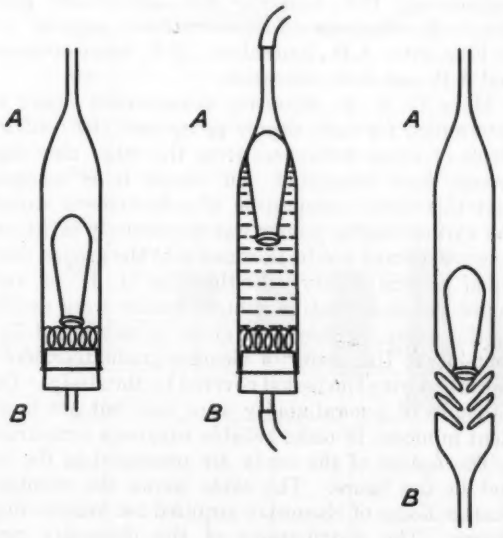
dents sometimes have difficulty in perceiving why the reactivity of this particular radical is not affected by resonance in the ring. With it, a comparison of the phenyl and benzyl (VIII) radicals becomes simple and instructive. Discussion of the conjugation of the ring with external unsaturated systems is also simplified, *e. g.*, the halobenzenes, the base strengths of anilines, and additions to benzoyl and cinnamoyl groups in ketones, esters, etc.

This method of presentation has been developed and tried over several years and found very satisfactory. The examples given here have been kept to a minimum and made fairly general; the instructor who is interested in the electronic approach to teaching organic chemistry can provide many more applications for himself.

## A SIMPLE VALVE TO PREVENT BACK SUCTION IN A VACUUM SYSTEM

**M. C. CHACO**
Indian Institute of Science, Bangalore, India

A SIMPLE, compact device has been worked out to prevent back suction of water from a water pump. The materials necessary for its construction are readily available in any laboratory.




I II III

It consists of a tapered glass tube of 10 cm. length and 2.2 cm. width, the wide end being closed with a one-hole rubber stopper carrying a glass tube as shown in I in the figure. A good ink filler nipple, about 4 cm. long and 1.3 cm. wide at the wide end, preferably coated with a thin layer of silicone grease, is placed inside, the closed end pointing to the tapered end of the tube. A roll of metal wire, rolled in the form of a spring fitted in between the nipple and rubber stopper, prevents the hole at *B* from getting closed during evacuation. The end *A* and the opening of the tube at *A* are finally closed as shown in II. It thus prevents water from passing into the system. The valve works best in the vertical position as shown. This also helps to drain away any liquid present inside the tube during evacuation. The nipple will last longer if kept clean and dry. Too much contact with vapors that easily attack rubber will spoil the nipple. III is a modification of the valve, in which the end *B* is constricted.

**ACKNOWLEDGMENT**

Thanks are due to Dr. B. H. Iyer and Dr. Sukh Dev for their kind encouragement.

# THE CHEMISTRY PROFILE OF THE GRADUATE RECORD EXAMINATION

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The University of Georgia, Athens, Georgia

THE Graduate Record Examination is the outgrowth of a research project in higher education initiated in 1936. The tests which comprise this examination were designed "to show the nature and extent of the advanced students' actual equipment in knowledge"[1] of broad subject matter fields of the typical undergraduate curriculum. The Graduate Record Examination results are at present endorsed or required by over 150 colleges and universities in the admission and guidance of graduate students. The G. R. E. profile tests which are taken by all University of Georgia graduate-school applicants cover the fields of chemistry, biology, physics, mathematics, social science, literature, and fine arts. Separate scores representing the student's standing with respect to his knowledge of the subject are reported for each field.

Since certain minimal undergraduate training is assumed and a baccalaureate degree is required for admission to graduate school, the question arises as to the effect of various undergraduate curricula on the several G. R. E. scores. Therefore, the purpose of this study was to investigate the relationships between scores on the G. R. E. profile tests and the kind and amount of undergraduate training of students with various baccalaureate degrees. The portion of the study reported here will deal only with chemistry profile scores of graduate students in relation to their undergraduate training in chemistry.

The 1807 graduate students who were in attendance at the University of Georgia between February, 1946, and February, 1952, were selected as subjects for this study. The group included all graduate students except some few irregulars who were not seeking advanced degrees. Because of the smallness of the samples ($N < 10$), students who had earned various infrequently awarded baccalaureate degrees were also omitted from this portion of the report. All seven professional schools and the five divisions of the College of Arts and Sciences were represented. In the base group men students outnumbered women by 1173 to 634. The mean age of the group was 31.76.

[1] "The G. R. E. and Returning Service Personnel," Carnegie Foundation for the Advancement of Teaching.

**Courses Required in Chemistry for Various Baccalaureate Degrees Offered by The University of Georgia**

| *Degree* | *Quarter hours of chemistry required* |
|---|---|
| B.S., agricultural engr. | 10 |
| B.S., forestry | 10 |
| B.S., agriculture | 10[a] |
| B.S. | 5[b] |
| B. Bus. Admin. | 5 |
| B. Fine Arts | 5 |
| A.B. | 5[b] |
| A.B., journalism | 5 |
| B.S., home economics | 10 |
| A.B. and B.S., educ. | 0[c] |

[a] Five additional hours science required, all of which may be chemistry.
[b] Ten additional hours science required, all of which may be chemistry.
[c] Five hours science required. Chemistry not specified.

## PROCEDURE

G. R. E. scores and other data were obtained from official records of the Dean of the Graduate School. The course requirements in chemistry were found by inspection of the General University of Georgia Catalogue and Registrar for the years covered by the study. The degree groups compared were: B.S., agricultural engineering; B.S., forestry; B.S., agriculture; general B.S.; B. Business Administration; general A.B.; B. Fine Arts; A.B., journalism; B.S., home economics; and A.B. and B.S., education.

Mean G. R. E. chemistry achievement scores were determined for each degree group and the confidence levels of mean differences from the other nine degree groups were computed. Of course it is recognized that this direct comparison of achievement scores of the various degree groups was not entirely satisfactory because it could not be assumed that the groups were of equal general ability. Neither the G. R. E. verbal factor nor quantitative subtest results were available on this group, as they were given to only about 15 per cent of the University of Georgia graduate-school applicants during the period covered by the study. Other measures of general ability were used but not in sufficient numbers to make reliable subgroup comparisons.

The results of the study are presented in the table and in the figure. The table shows the number of quarter hours of chemistry required for various degree groups. The distributions of the chemistry profile scores for the ten baccalaureate degrees are shown in the figure.

From an examination of the figure it is seen that with respect to proficiency in chemistry the ten degree groups roughly form three clusters or subgroups made up of science, nonscience, and education majors. That

is, graduate students who have undergraduate degrees in agriculture, including the agricultural engineering and forestry, have a better knowledge and understanding of the basic principles of chemistry than students from other curricula. These three groups and the straight B.S. students are significantly (0.01 level of confidence) better in chemistry than all the other degree groups. The second major cluster is composed of B.B.A., fine arts, straight A.B., journalism, and home economics majors. The means of the last four degree groups are separated by only four-tenths of a standard score point but only the B.B.A. and the straight A.B. students are significantly better than the last cluster. Education majors, who compose the second largest degree group, are the most poorly prepared in chemistry.

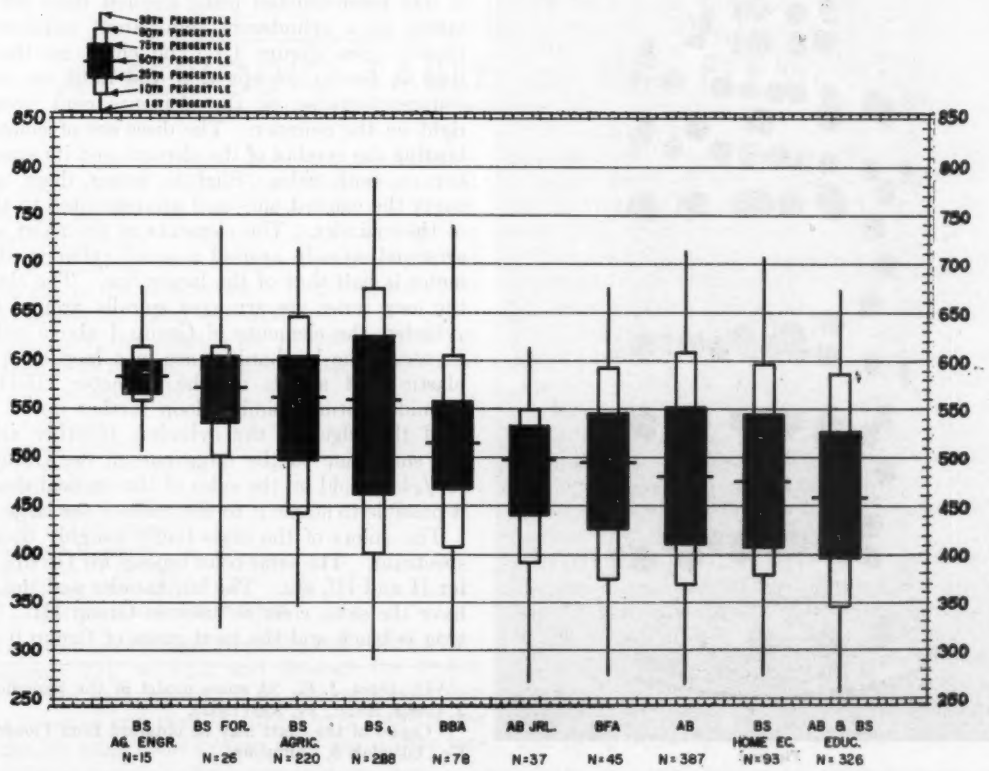
## DISCUSSION AND SUMMARY

The college "course for credit" is believed by some educators to have been designed by university administrators as a bookkeeping expedient and actually to have little relation to specific knowledge and understanding of the subject. There is some evidence[2] that taking biology, chemistry, and physics courses beyond a certain minimum has little or no effect on such examinations as the science test of the Medical College Admission Test, but there is almost a complete lack of direct data concerning those students who have had no chemistry or those who are required to take only one, two, or three courses. A question also arises as to the performance of these students on the G. R. E., which does not purport to cover specific "courses" but tests the student "on the content of his mind, on what he has learned and retained because he has learned it well."[3] Is there a relationship between G. R. E. chemistry scores and the number of required undergraduate courses in chemistry? The results presented in the previous section would seem to indicate that such is the case. That is, mean chemistry achievement, with one exception, decreases significantly for the various degree groups as the number of required chemistry courses decreases. The exception is home economics. Although ten quarter hours of chemistry are required for this degree, home economics majors scored only slightly better in chemistry than the education majors, of whom no course in chemistry is required. Other evidence available, but not presented here, would seem to indicate that this effect is not the result of sampling errors or artifacts.

On the basis of the facts presented above it would also seem reasonable to assume that the chemistry pro-

[2] SCHULTZ, D. G., "The relationship between scores on the science test of the Medical College Admission Test and amount of training in biology, chemistry, and physics," *Educational and Psychological Measurement*, 11, 138–50 (Spring, 1951).

[3] *Ibid.*




Distribution of G. R. E. Chemistry Profile Scores of University of Georgia Graduate Students with Various Baccalaureate Degrees

file test of the G. R. E. measures the content of the basic chemistry courses required of University of Georgia undergraduates. Since course content frequently varies from university to university and sometimes even from quarter to quarter within the same university, the findings should not necessarily be expected to hold for other subject matter tests, for other groups, or for any individual student.

# A CUT-OUT CHART OF THE PERIODIC SYSTEM

**JENNIE E. CLAUSON**
Glendale High School, Glendale, California

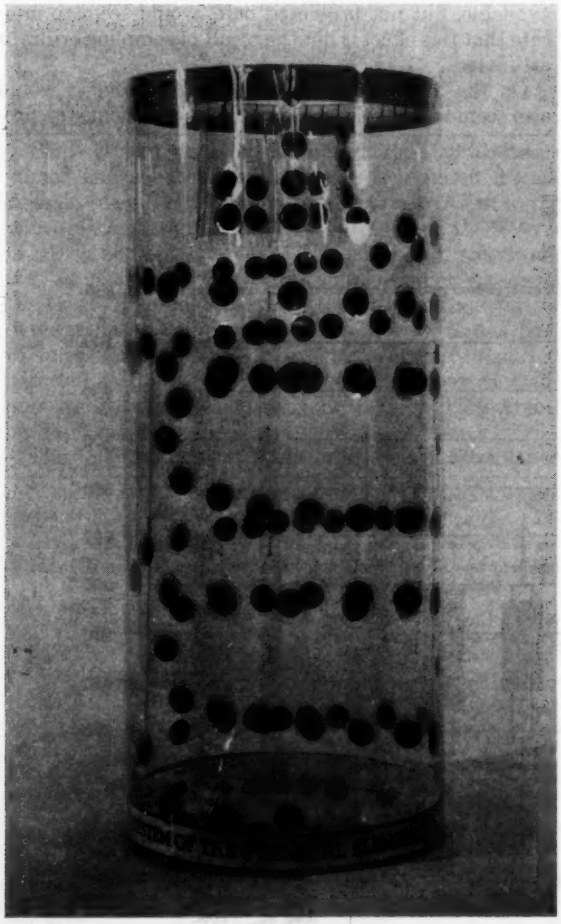


Figure 1

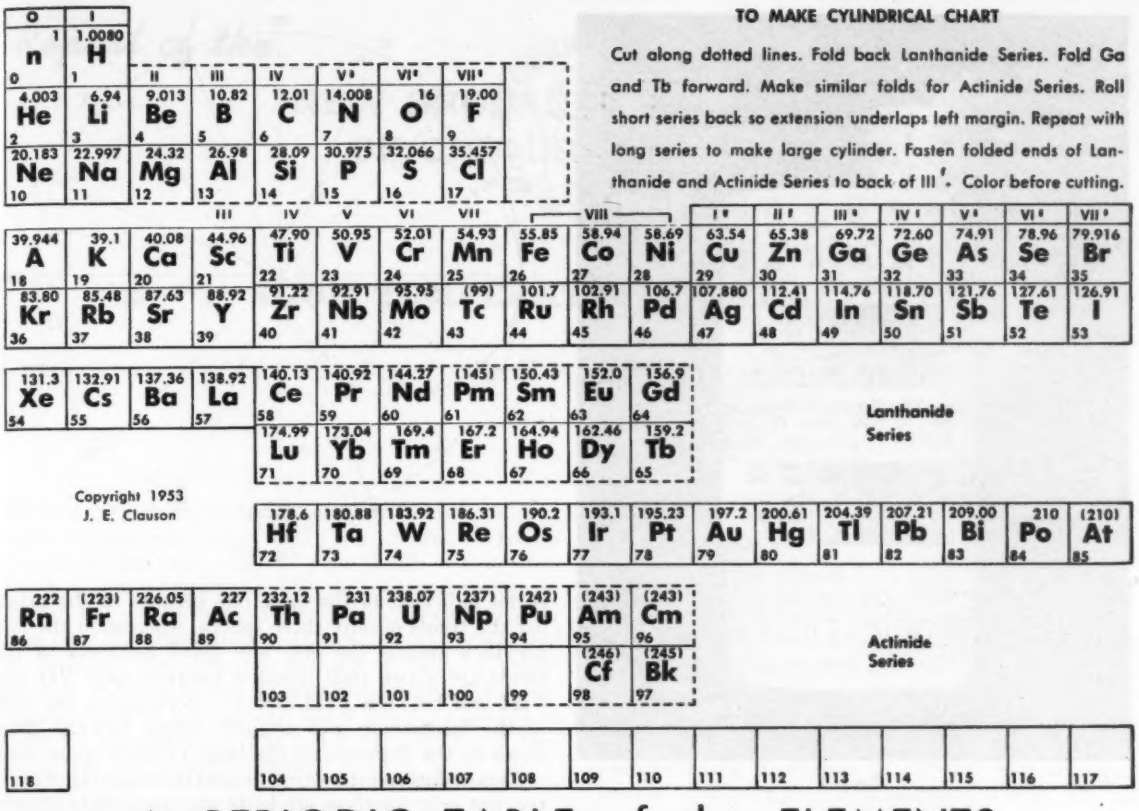
THIS chart was constructed to make available for student use the three-dimensional idea incorporated in the space model of the periodic system made in 1951.[1,2]

To overcome the fragility and instability of the previous model, which had wooden balls on a wire spiral, it was reconstructed using colored discs for the elements on a cylinder of transparent cellulose acetate plastic. (See Figure 1.) The chart on the circular base is similar, except that the radii are numbered counterclockwise, so the elements read from left to right on the cylinder. The discs are of colored paper bearing the symbol of the element and its atomic number on both sides. Slightly larger discs of plastic cover the colored ones and are cemented to the inside of the cylinder. The elements of the short series are arranged spirally around a small cylinder whose diameter is half that of the larger one. The elements of the long series are arranged spirally around the large cylinder, the elements of Group I above radii I and I′, etc. The lanthanides are in a loop on a sheet of plastic that stands on the diameter III-III′. The actinides form a similar loop farther down. Staples hold the edges of the cylinders together and fasten the small one to the large one on the Group 0 line. A 1/4-inch fold on the sides of the vertical sheet makes it possible to staple it to the walls of the large cylinder.

The colors of the discs follow roughly those of the spectrum. The same color repeats for Groups I and I′, for II and II′, etc. The lanthanides and the actinides have the same color as color as Group III. The neutron is black and the inert gases of Group 0 are gray.

[1] CLAUSON, J. E., "A space model of the periodic system," J. CHEM. EDUC., 29, 250 (1952).

[2] Copies of the chart may be obtained from Pioneer Printing Co., Glendale 5, California.


TO MAKE CYLINDRICAL CHART
Cut along dotted lines. Fold back Lanthanide Series. Fold Ga and Tb forward. Make similar folds for Actinide Series. Roll short series back so extension underlaps left margin. Repeat with long series to make large cylinder. Fasten folded ends of Lanthanide and Actinide Series to back of III′. Color before cutting.
Lanthanide Series
Actinide Series
Copyright 1953 J. E. Clauson

# A PERIODIC TABLE of the ELEMENTS

Figure 2

Even this model is fragile and took considerable time to assemble. To make the three-dimensional idea available for student use, a chart was made with the elements arranged in the order shown in Figure 2 so there is continuity without interruption at 57 and 89 and no gap in the short series. To get it on a sheet $8\frac{1}{2} \times 11$ inches the spiral was sacrificed.

Students color the chart with pencils such as are used in their map making. The following color scheme worked out satisfactorily:

Group 0 uncolored
Groups I and I′ purple
Groups II and II′ blue-violet
Groups III and III′ blue
Lanthanides and actinides blue
Groups IV and IV′ green
Groups V and V′ yellow
Groups VI and VI′ orange
Groups VII and VII′ red
Group VIII triads line-shaded in black.

Scissors were used to cut from the right edge above the numerals VII′ to VIII and through the broken line below the short series. The rest of the broken line was followed and then the line above I and 0 was cut to the left edge. The broken lines around the lanthanides and the actinides were cut with a sharp knife or razor blade. These strips were folded back at the left edge. The last two elements of the double strips were folded forward.

Glue was placed on the right margin of the chart, which was then rolled to make a cylinder, lining up the left edge against Group VII′. Similarly, the short series were rolled into a small cylinder at the top. These edges may be fastened with staples if preferred. Glue was placed on the back of the tab at the end of the lanthanide strip to fasten it inside the cylinder in line with Group III′. The same was done with the actinide strip. The margin at the overlapping of the cylinders may be left empty; students may write in the arabic numerals at the beginning of each series. The finished model is shown in Figure 3.

From carbon through fluorine and from silicon through chlorine the elements are in groups marked with the Roman numeral prime because their projections fall on the prime radii of the circular chart on the base of the large models. Carbon and silicon are directly above the center of the large circle. Figure 4 shows a projection of the first short series and the first long series. The group numbers V and V′, VI and VI′, etc., do not

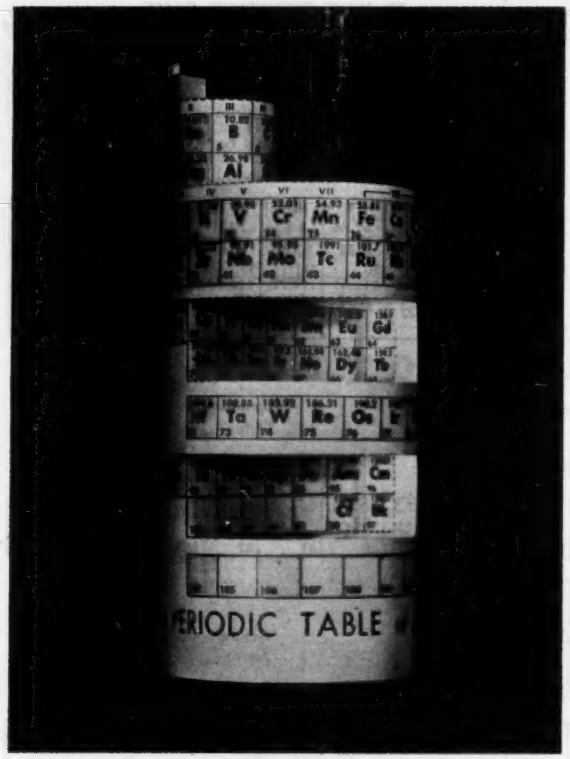



Figure 3

have the same significance as V-A and V-B,VI-A and VI-B as used on other charts of the periodic system. In the paper model the diameter of the small cylinder

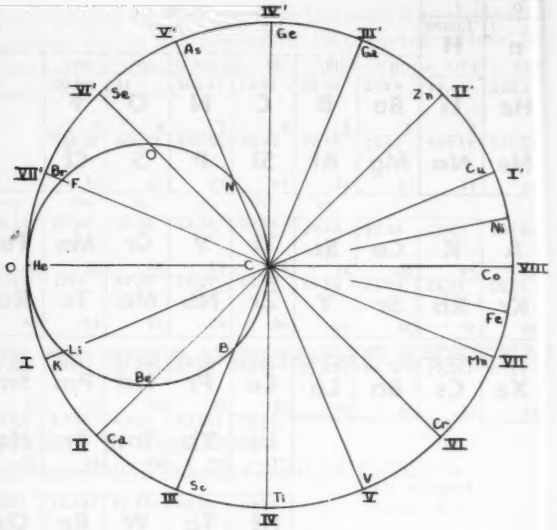



Figure 4

is not half that of the large one because in the printing the triads occupy three spaces, whereas in the two previous models the first and third members of the triads are above radii inserted between radii VII and VIII and between VIII and I′. By turning the ends of the lanthanide and actinide strips forward these series fit the diameter of the large cylinder quite well.

This makes an interesting project in beginning chemistry, not only for those students who appreciate theory, but for those who need to use their hands to help them to learn. They contribute to making the finished product and have the model as a memento of their chemistry course.

## ARE YOU USING THE NRC CHEMICAL CODE?

THE Chemical-Biological Coordination Center of the National Research Council is very interested in learning of other organizations who are now using or are planning to use their "Method of Coding Chemicals for Correlation and Classification." This extensive code was devised primarily to permit the use of punched cards in the correlation of chemical structure with biological activity. Proof of the adaptability and versatility of the code is some 53,000 compounds now coded by the Center. The Center would like to know of the experience others have had in adopting the code for their own special needs and also would be glad to answer any questions. Please address all correspondence to Miss Estaleta Dale, Chemical-Biological Coordination Center, National Research Council, 2101 Constitution Avenue, Washington 25, D. C. Copies of the code may be obtained from the Publications Office, National Research Council, 2101 Constitution Avenue, Washington 25, D. C. ($1.50).

*Report of the*

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

# HIGH TEMPERATURE REFRACTORIES[1]

**O. J. WHITTEMORE, JR.**
Norton Company, Worcester, Massachusetts

REFRACTORIES are materials capable of withstanding high temperatures, say 1000°C. or better. The refractories that will come to your minds will be firebrick in furnaces and crucibles for melting substances. I shall tell you of many unusual refractories, including one used in your kitchen, of another as radioactive as uranium and with the density of lead, of others capable of being heated to high temperatures in a few seconds, and of a refractory which has been heated to 2500°C. commercially, has twice the density of firebrick, yet is a better insulator.

## CERAMICS

Before getting into my subject too deeply, however, I should like to tell about the ceramics field, of which refractories are one part. Probably the word ceramics means art pottery to most of you. Pottery is but one small part of the package—the gilt wrapping. The china on your table are ceramics. The porcelain enamel coatings on your refrigerators and bathtubs, the glass in your windows, the brick in your houses, perhaps even the teeth in your mouth are ceramics. The filaments in your radio tubes may be ceramic-coated and the envelope may be a glass sheath. Your radio circuits are insulated with ceramics, and new ceramic capacitors—the titanates—are undoubtedly present. The major classifications are: abrasives, refractories, glass, whitewares, porcelain enamels, cements and plasters, and structural clay products.

The ceramics industry was once defined as the clay-working field, but this definition is inadequate today because many ceramics contain no clay. Ceramics might be defined as inorganic materials converted by heat to usefulness. This difficulty of definition is caused partly by the growing interrelation of fields. The organic chemists have developed silicones, which are close to silicates, and have also attached organic radicals to the clay bentonite, and call the product "bentone." A new group of materials called "cermets" are combinations of ceramics and metals.

## CERAMIC ENGINEERING

As scientific educators, you will be interested in curricula available in ceramics. Ceramic engineering degrees have been granted for over 50 years, the first school being Ohio State, which is quite logical since Ohio ranks first among the states in value of ceramic products. There are now about 15 schools offering studies leading to degrees in ceramic engineering or ceramic technology. Unfortunately, there are no New England colleges that offer a full curriculum, but graduate study can be pursued at the Massachusetts Institute of Technology, where some of the most advanced work is being carried on under F. H. Norton. At the University of New Hampshire, ceramic art courses are offered. Many other colleges, schools, and other groups throughout the country are giving art pottery studies.

Ceramic engineering courses include basic engineering studies with two to three years of chemistry, geology, and mineralogy, and the ceramic studies such as properties of ceramic materials, pyrometry, and studies of particular fields.

The jobs that ceramic engineers do are quite similar to those of chemical engineers—research, development, control, manufacturing supervision, and sales—except that, of course, the jobs are in the ceramics rather than the chemicals industry. At the present and ever since World War II, there has been a serious shortage of ceramic engineers, as there has been in all scientific pursuits. The deficiency is probably greater in ceramics because the field is not so well known. In one excellent college this year, *not one freshman* enrolled for ceramic engineering. Many manufacturers have had to employ graduates in other engineering fields because ceramic engineers were not available, and have had to supplement their education.

I can recommend ceramic engineering highly as a field in which students with scientific and engineering

[1] Presented at the 273rd Meeting of the New England Association of Chemistry Teachers, Brandeis University, Waltham, Massachusetts, December 5, 1953.

ability can find interesting and fruitful employment. It is a field rapidly becoming more and more complex, yet has many traditions, and is one of the few technical fields in which art has a place.

The American Ceramic Society, organized 55 years ago, is our technical society, and holds annual, divisional, and sectional meetings and publishes a *Journal*, a *Bulletin*, and *Ceramic Abstracts*. Two internal groups are the National Institute of Ceramic Engineers and the Ceramic Educational Council. Information can be obtained from The American Ceramic Society, 2525 North High Street, Columbus 25, Ohio.

## HIGH TEMPERATURE REFRACTORIES

Besides the business expansion since World War II, several other factors have contributed to the current growth and importance of ceramics. Radar and television required better insulators and capacitors. In addition, emphasis began to be placed on higher and higher temperatures and other severe operating conditions. The atomic energy program required containers to melt and refine the new metals and construction materials for nuclear reactors. Jet propulsion will achieve much higher efficiency at higher temperatures than now possible with metals, so much work is being devoted to ceramics. So now I return to my subject—high temperature refractories.

The first refractories were rocks and bricks that man used to refine metals and to build fireplaces. As time went on he found by experience that certain rocks were more refractory, that certain clays made better firebrick. He found that *quartz* ($SiO_2$) is a good refractory if heated carefully and that *kaolin* ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) was one of the most refractory clays. Much later, he found that the minerals *magnesite*, *chromite*, and *dolomite* were very useful refractories for steel melting. About this time (the end of the nineteenth century), chemistry and physics began to help him to understand his materials, to show him how to purify them for greater value.

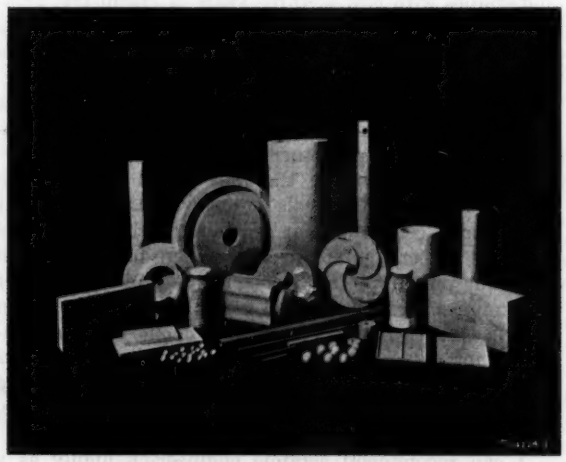


**Figure 1. Stabilised Zirconia Refractory Shapes**

About this same time, another industry was developing—the abrasives industry—which was interested in hard materials. In general, the very hard materials are also refractory. Fused alumina and silicon carbide are the two common abrasives today but they also furnish the backbone of the special refractories industry.

Silicon carbide has very high thermal conductivity (a silicon carbide brick conducts heat seven times better than a fireclay brick). It also is very resistant to thermal shock, because of its high conductivity and relatively low thermal expansion. Of all the carbides it is the most resistant to oxidation. Silicon carbide bricks are strong at high temperatures and are resistant to coal ash slags. They are used to construct muffle walls where high heat transfer is necessary and to line water-gas generators and boiler furnaces where heat shock resistance and slag resistance are required. Silicon carbide plates are used in the whitewares industry for supporting the ware during firing.

Silicon carbide conducts electricity, and rods are made from it to heat furnaces to 1450°C. in air atmosphere, or several hundred degrees above the use temperature of wire-wound furnaces. One spectacular use of silicon carbide refractories is as nozzles for experimental rockets. This is a refractory that can be heated to high temperatures in a few seconds.

Fused alumina has great refractoriness (melting point 2015°C.), has good chemical stability, is an excellent electrical insulator, and has relatively high thermal conductivity. As chemists, you are familiar with fused alumina filtering crucibles and cores for wire-wound furnaces. The chemical industry has been developing high temperature gas synthesis processes since World War II and fused alumina "pure oxide" brick have been used for the furnace linings because of their high refractoriness and resistance to atmospheres which would reduce silicate-bearing refractories.

## PURE OXIDE REFRACTORIES

The "pure oxide" class of refractories is relatively new and includes those refractories essentially of one oxide, free particularly from glass-forming silica. Phase diagrams show in most cases that highest melting points can be realized with no contaminant or other oxide. However, the presence of a small amount of silica not only lowers the melting point of a refractory but also forms glass which reduces the load-bearing capacity to a greater extent than would be expected by a study of the phase diagram. Clay-bonded fused alumina brick increase in thermal conductivity with temperature in comparison with self-bonded or recrystallized fused alumina brick, which decrease in thermal conductivity with temperature.

Alumina, $Al_2O_3$, magnesia, MgO, and stabilized zirconia, $ZrO_2$, are the three important "pure oxide" refractories. Magnesia has a very high melting point (2800°C.) but has high vapor pressure above 2200°C. and cannot be used in reducing atmospheres above 1700°C. One new application for magnesia is in a furnace for the fixation of atmospheric nitrogen by

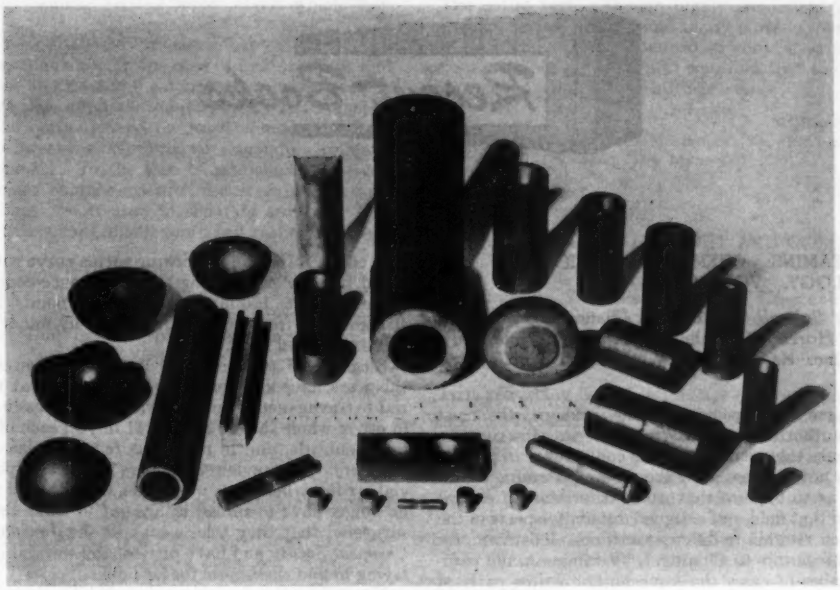


Figure 2. Boron Carbide Shapes

merely heating air to 2200°C. Magnesia is a very important refractory for metal-melting or purification because of its great resistance to basic slags. Fused magnesia is the special refractory used in your kitchen in the sheathed electric stove heaters. These contain fused magnesia because of its high electrical resistivity and thermal conductivity.

Stabilized zirconia refractories contain about five per cent lime, CaO. Pure $ZrO_2$, when heated, inverts from a monoclinic to a tetragonal crystal form at about 1000°C. This transition is accompanied by a large volume contraction, which usually cracks up any refractory shape. When about five per cent CaO is fused into solid solution with $ZrO_2$, a new cubic crystal is formed which does not invert when heated. However, by allowing a small residual amount of the monoclinic form to remain present, the over-all thermal expansion is lowered. Stabilized zirconia refractories, therefore, require careful control to insure the proper crystal content. To my knowledge, this is the first refractory for which such control has been required. Quantitative crystal analyses can be readily made with X-ray equipment.

Stabilized zirconia is the refractory I mentioned which has been used commercially in furnaces at 2500°C. for gas synthesis. A number of stabilized zirconia refractory shapes are shown in Figure 1. This refractory has twice the density of fireclay brick, yet is a much better thermal insulator. It is relatively expensive but makes possible processes for which suitable refractories have not been available before.

**Properties of New Special Refractories**

| *Name* | *Formula* | *Density* | *Melting point, °C.* | *Thermal conductivity, Cal./sec./cm.² cm./°C.* |
|---|---|---|---|---|
| Zirconium carbide | ZrC | 6.73 | 3540 | 0.049 |
| Titanium carbide | TiC | 4.93 | 3140 | 0.041 |
| Silicon carbide | SiC | 3.217 | 2600[a] | 0.10 |
| Boron carbide | $B_4C$ | 2.50 | 2450 | 0.065 |
| Titanium boride | $TiB_2$ | 4.50 | 2900 | 0.06 |
| Zirconium boride | $ZrB_2$ | 6.085 | 3060 | 0.057 |
| Chromium boride | CrB | 6.17 | 2760 | ... |
| Molybdenum disilicide | $MoSi_2$ | 6.24 | 1850 | ... |

[a] Decomposes.

## OTHER SPECIAL REFRACTORIES

Active research and development work is being conducted by the special refractories industry on many other unusual refractories. These include: *Boron carbide* ($B_4C$); used primarily because of great hardness and wear resistance, this compound has a melting point of 2450°C. Its high boron content (70 to 85 per cent) is the reason for its use in nuclear reactors as a neutron absorber. Articles made of boron carbide are shown in Figure 2. *Thoria* ($ThO_2$); this is the refractory I mentioned that has the density of lead and is as radioactive as uranium. Thoria has the highest melting point of all oxides (3300°C.) and is less reactive at high temperatures than other oxides. Metallic titanium has been melted successfully on a small scale in thoria crucibles. *Boron nitride* (BN); dissociation temperature is 3000°C. It is an excellent high temperature lubricant and a thermal and electrical insulator. It has the appearance of graphite except for its white color.

Many other refractory compounds are being prepared and tested; several are cited in the table, together with some of their properties.

## THE VITAMINS: CHEMISTRY, PHYSIOLOGY, PATHOLOGY. VOLUME I

**Edited by *W. H. Sebrell, Jr.*, Director, National Institutes of Health, and *R. S. Harris*, Massachusetts Institute of Technology. Academic Press, Inc., New York, 1954. xiii + 676 pp. 15 × 23 cm. $16.50.**

THIS three-volume work as projected is, perhaps, the most ambitious of the authoritative efforts to treat vitamins comprehensively. To secure the greatest possible competence in presentation, the editors not only assigned the several vitamins to different authors so as to be sure that each writer was an experienced researcher in that field, but assigned different aspects of the presentation of each vitamin to different authors. There are, for example, eight contributors to Chapter I, "Vitamins A and carotenes." In a number of cases the same author writes parts of several chapters. R. S. Harris gives "Nomenclature and formulas" for each of these four: vitamins A, ascorbic acid, $B_{12}$, and biotin, which comprise the material of Volume I.

The editors seem to have been successful, in the main, in avoiding the bane of producers of works by various contributors, *viz.*, variability in style of presentation. Actually, fairly uniform methods of selection of material, relative detail of description, and balance between fundamental biochemistry (metabolic reactions, etc.) and practical matters (proper handling to avoid losses, etc.) seem to prevail in each chapter. About the same relative prominence of historical matter, adequate but not too wasteful of words, also prevails.

This work will undoubtedly be of great use to all nutrition workers and other biochemists. One awaits with much interest publication of the two other volumes.

PHILIP H. MITCHELL

BROWN UNIVERSITY
PROVIDENCE, RHODE ISLAND

## ● VAPOR PRESSURE OF ORGANIC COMPOUNDS

***T. Earl Jordan*, Publicker Industries, Inc., Philadelphia, Pennsylvania. Interscience Publishers, Inc., New York, 1954. ix + 226 pp. 165 figs. 21 × 28 cm. $14.50.**

THIS volume is probably the most elaborate and elegant compilation of vapor pressure-temperature data that has ever been published. Any library which has this work, the Stull tables (*Ind. Eng. Chem.*, 39, 517 (1947)), and the Dreisbach tables for general types of compounds (*cf.* THIS JOURNAL, 29, 638 (1952)) may well claim practically complete coverage of significant $p$-$t$ tabular information on pure organic compounds to date.

The ten chapters include over 1500 specific compounds, for each of which is given name, formula, $p$-$t$ values, literature reference, and entry in general alphabetical index. In addition, for each compound the particular modification of the log $p = A - B/T$ equation, appropriate to the example, is given when available. Finally, the $p$-$t$ graph for each is drawn on a full-page plate, usually in company with several other graphs for economy in reproduction. In these plates the classical log $p$-reciprocal of $T$ graduation seems to have been used, but with the $1/T$ scale reversed, most conveniently, and marked left to right in Centigrade degrees.

The author has noted—as many people do not—that a log $p$-$1/T$ plot in most cases yields not a straight line, but instead a "drooping" curve. Instead of drawing such a curve with a spline, he has saved time by pinpointing a few reference coordinates, *e. g.*, the 1 mm., 10 mm., 100 mm., and 760 mm. points, and then drawing straight lines from point to point. Only minor errors arise from this economical trick.

Elegance of typographical layout and convenience in use of this work have unfortunately been attained at the cost of editorial extravagance. Space is wasted in excessively wide margins, in use of whole sheets (8 ½ × 11 in.) on each of which is nothing but a subtitle, and in numerous redundancies of vapor-pressure numbers. The reviewer wonders if offset publishers, whose special art in earlier years was crude, have not yet realized that they no longer have to spread things out to make them legible. It is suggested that they take a look at the *Journal of the American Chemical Society* and have pity for the worried chemical librarian trying to find shelf room for fat books.

Not only is this a good example of high-class offset publication, but particular praise is due for excellent workmanship on the plates. Although a few errors were noted, these are in the editorial blemish class and would not interfere with use of the book.

G. ROSS ROBERTSON

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

## ● ORGANIC CHEMISTRY: A BRIEF COURSE

***Robert Ward Getchell*, Professor of Chemistry Emeritus, Iowa State Teachers College. McGraw-Hill Book Co., Inc., New York, 1954. viii + 278 pp. 9 figs. 8 tables. 16 × 23.5 cm. $4.**

THERE are not a large number of organic texts specifically designed for the one-term course. Of those available many are unsatisfactory from the standpoint of the choice of material included and the treatment of the subject matter. This particular text has little either to commend or condemn it. While most of the traditional material of a regular organic chemistry course is covered, few topics are treated with sufficient depth or skill to either whet or satisfy the intellectual curiosity of the average student.

In addition to topics commonly treated in such a text, there are sections on plastics, rubber, proteins, polynuclear and heterocyclic compounds, vitamins, enzymes, hormones, and medicinals, which constitute more than one-third of the textual material. These sections are chiefly a compilation of products and uses with very little space devoted to the chemistry involved or to the relation of these materials to the various classes of organic compounds.

This reviewer feels that there is a definite need to reconsider the purpose of the so-called "short courses" and the texts to be used by students taking these courses. Since such courses constitute a considerable part of the student's contact with science, it would appear logical to treat a few selected topics as thoroughly as is commensurate with the students' background and thus send the students into their respective fields, such as agriculture, homemaking, and the arts, with the assurance that chemistry is a systematic although incomplete body of knowledge. The students may not "learn about" many things but they will "learn" something.

Students using this text as a guide for a one-term course will probably be left with the conception that organic chemistry is an

endless succession of vaguely related topics about which they remember little.

An attempt has been made to "integrate" the aliphatic and aromatic series of compounds. In the case of hydrocarbons and alcohols and phenols, the aromatic compounds are discussed in the chapter following their aliphatic counterparts. In the case of aliphatic halides and carbonyl and carboxyl compounds, from one to four chapters intervene before the corresponding aromatic compounds are discussed. In the case of nitrogen derivatives, aliphatic and aromatic compounds are discussed in the same chapter, although they are treated in separate sections. The student may find this arrangement confusing rather than enlightening.

The format of the book is traditional. No spatial representations or photographs are used. The questions are good and in many cases are thought-provocative. The use of cross references within the text is a helpful feature which should be more widely adopted.

WILLIAM B. COOK

BAYLOR UNIVERSITY
WACO, TEXAS

## GENERAL CHEMISTRY: A TOPICAL INTRODUCTION

*Eugene G. Rochow* and *M. Kent Wilson*, Department of Chemistry, Harvard University. John Wiley & Sons, Inc., New York, 1954. xiii + 602 pp. Many figs. 15.5 × 23.5 cm. $6.

THIS unusual text for college freshmen makes no attempt to cover the entire field of general chemistry. The authors believe most current texts include more material than is necessary, and so they have carefully selected certain topics which they think are adequate for a sound fundamental training in general chemistry. Chemical principles are stressed throughout, and are related, as far as possible, to personal experiences of the student. The descriptive details in such chapters as, The Sea as a Chemical Storehouse, Photochemistry, Piezochemistry, Biochemistry, Macromolecules, and Our Resources, are not only of general interest, but also provide excellent illustrations of chemical principles.

A number of mathematical derivations, not commonly given in general chemistry texts, are included. The authors do not expect the student to be able to reproduce these, but introduce the derivations as a means of illustrating how certain generalizations are reached.

The illustrations by Maryellin Reinecke are small, but for the most part excellently done. However, only four photographs are included in the text.

The exercises given at the ends of all but two of the chapters are good, but are relatively few in number. The reviews of chemical arithmetic, mathematical concepts, and operations given in Appendixes II and III are so brief and condensed that many students will need to use a book of chemical calculations along with the text. References to such a book are given. Answers to the numerical problems are given in Appendix III.

The authors only occasionally use the historical method of introducing a topic. Their experience has led them to believe that a more direct approach, utilizing personal experience and modern evidence, is better. However, a short, well written history of the development of the ideas of chemistry is given in Appendix I.

Typographical errors are few, but in common with most texts, a few inaccuracies and inconsistencies appear. The International Union of Chemistry (page 10) is now called the International Union of Pure and Applied Chemistry. The values for the heats of formation of the gaseous hydrogen halides, given on page 195, are in error, as is the value of the $K_{sp}$ for $Al(OH)_3$ (page 222). The $K_{sp}$ value given for AgS in the same table is evidently intended for $Ag_2S$. The authors recommend the use of partial ionic equations (page 75), yet use the molecular forms of $Na_2CO_3$, $NaHCO_3$, and $NaC_2H_3O_2$ in the hydrolysis equations given on page 168.

The entire text, although highly condensed in parts, is well written and students will find many parts extremely interesting. The book can be recommended to those instructors who teach serious, capable students, and who find that the topics included will meet the requirements of their course.

MORRIS F. STUBBS

NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY
SOCORRO, NEW MEXICO

## THE NATURE OF LIGHT AND COLOUR IN THE OPEN AIR

*M. Minnaert.* Translated by *H. M. Kremer-Priest.* Revised by *K. E. Brian Jay.* Dover Publications, Inc., New York, 1954. xi + 362 pp. 160 figs. 42 plates. 13.5 × 20.5 cm. Paper, $1.95. Cloth, $3.95.

IT IS refreshing indeed in this age of "flying saucers," when so many natural phenomena are given a supernatural or unearthly explanation, to review this book by Prof. M. Minnaert of the University of Utrecht. Here are the subjects of environmental optics and physiological optics in popular form, written so that anyone who cares to look and think can observe and understand the curious, the beautiful, the bizarre, and the spectacular phenomena that occur almost daily in our lives.

"The Nature of Light and Colour in the Open Air" should be especially popular among boys who are interested in natural science.

JOHN E. TYLER

VISIBILITY LABORATORY
SCRIPPS INSTITUTION OF OCEANOGRAPHY
SAN DIEGO, CALIFORNIA

## ORGANIC COATING TECHNOLOGY. VOLUME I: OILS, RESINS, VARNISHES AND POLYMERS

*Henry F. Payne*, Technical Editor, American Cyanamid Company, and Adjunct Professor, Polytechnic Institute of Brooklyn. John Wiley & Sons, Inc., New York, 1954. vi.i + 674 pp. Illustrated. 16 × 23.5 cm. $10.

IT IS seldom that one with a broad background in an industry is able to prepare an integrated series of books on the industry without the aid of collaborators for the various chapters. In this case, the author is not only skilled in the art but also is presenting the material to students in college course work. The combination cannot fail to produce an outstanding pair of books.

Although in his preface the author states that the book is intended for students in paint courses and for new employees in the oil, resin, pigment, and paint industries, it is far more applicable than these groups would indicate. It presents the fundamentals and their application to a variety of chemicals whose use is broader than the organic coating industry. The initial chapter on the fundamentals of film formation gives the essentials of functionality and polymerization, the basis of the organic coating. The second chapter is an extensive description of the vegetable and marine drying oils that are used for film formation, their composition and treatment for use in coatings, and finally the mechanism of drying for film formation. Four chapters discuss other raw materials, volatile solvents, driers, varnish resins, and plasticizers. Varnish manufacture and utilization are treated in a short chapter.

Seven chapters discuss the various types of synthetic resins used in coatings: Alkyd, urea- and melamine-formaldehyde, rubber, cellulosic, vinyl, acrylic ester, and silicone resins. Each chapter is an excellent discussion of the fundamental chemistry of the class of resins, the method of manufacture, and the particular types used in organic coatings. Obviously the discussion of a resin cannot be complete with information on molding resins and technique. A final chapter on test methods of the coating indus-

try gives the standard tests for raw materials and performance of final product.

As a textbook this book will be excellent. Its use as a reference book will be far greater to the chemist for its clear presentation of fundamental chemistry of oils and resins, and their behavior under the conditions of surface coatings. The book is highly recommended, both as a text and as a general reference book.

KENNETH A. KOBE

UNIVERSITY OF TEXAS
AUSTIN, TEXAS

## ● CELL CHEMISTRY: A COLLECTION OF PAPERS DEDICATED TO OTTO WARBURG ON THE OCCASION OF HIS 70th BIRTHDAY

**Edited by *Dean Burk*, National Institutes of Health, Bethesda, Maryland. Elsevier Publishing Co., Houston, Texas, 1953. 362 pp. 155 figs. 86 tables. 16.5 × 25 cm. $7.50.**

WHEN on the occasion of a significant anniversary of a famous scientist his former students, co-workers, and friends are called upon to dedicate to him a volume of collected papers, some of them seize this opportunity to review salient points of their own work and perhaps to draw meaningful conclusions from them. Others just contribute a good piece of new experimental work which they happen to have at hand. Such is the collection of papers in the present volume. Led by an excellent biographical sketch of Professor Warburg, by Dean Burk, 36 articles present a varied and not very coherent account of current trends in the biochemistry of the cell. Among the authors are represented some of the most prominent chemists and physiologists of our day from all over the world. The original edition of this book appeared as an issue of *Biochimica et Biophysica Acta*, **12**, No. 1/2 (1953), and the reader interested in specific papers from this collection may want to refer to that journal. The subject matter, too varied to be stated here in full, ranges from pure organic chemistry of substances of interest in cell reactions, through photochemical and electrochemical studies of energy cycles and maximum quantum yields, to more traditional enzymatic reactions, their paths and mechanisms and experimental behavior. There are several articles on the physical chemistry of biochemical materials and on inorganic and organic model compounds of such materials. The papers are written either in English, French, or German; at the end of each article is found a brief summary in all three languages. Print and paper are excellent, and the book is attractively bound. There is an author and subject index.

The reader who wishes to gain a knowledge of cell chemistry will find this book hard going. The terse style of the original journal articles is addressed to the specialist. Although he will get an idea of current efforts in this field, the utter lack of transition from one of the papers to another will not give him a coordinated picture of present knowledge. The specialist who reveres the great work of Otto Warburg will find this collection a useful reference volume.

ALFRED BURGER

UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

## ● MAGNETIC COOLING

***C. G. B. Garrett.* Harvard University Press, Cambridge, Massachusetts, and John Wiley & Sons, Inc., New York, 1954. x + 110 pp. 13 figs. 14.5 × 22 cm. $4.50.**

THIS little book is one of the Harvard Monographs on Applied Science which are designed to present the results of current research. It includes a discussion of the techniques for obtaining and measuring temperatures below one degree Kelvin and treats briefly the thermodynamics of magnetic systems and the theory of the paramagnetism of crystals. The properties of various salts as revealed by adiabatic demagnetization experiments are reviewed; there is a chapter on magnetic cooperative effects; and in the final chapter the use which has been made of the magnetic cooling method for investigating the properties of materials at very low temperatures and in obtaining the partial alignment of nuclei for experiments in nuclear physics is discussed.

Dr. Garrett's book is similar in scope to the monograph "Magnetism and Very Low Temperatures" by H. G. B. Casimir, which was published in 1940, and most of the emphasis in the present volume is on developments that have occurred since that date. As is to be expected in a monograph of this sort, the author draws heavily from his own work and that of the English school, but he also discusses, though evidently with less familiarity, recent work in Holland and the United States.

The book is authoritative and quite free from errors. There are some points in which this reviewer does not agree with the author, such as the statement (page 32) that there is a serious magneto-resistance effect in carbon thermometers, or the definition of adiabatic susceptibility as that which is measured when the frequency is great compared to the spin-lattice relaxation time (page 31). The author states that "The literature on the subject of the thermodynamics of magnetization is rather confusing," and the treatment given by the author will, I fear, leave many readers still confused. Fortunately, the final thermodynamic equations obtained are equivalent to those derived in the simpler treatment used by Keesom, Giauque, and Casimir.

The level of the book is such that it can be read with profit by a graduate student in physics or physical chemistry. A large amount of material is covered in a few pages and the treatment is necessarily condensed, particularly in the theoretical discussions. The book is the first to treat the field of adiabatic demagnetization since the appearance of Casimir's monograph and every specialist in the field will want to read it. It is also recommended as an introduction to and general survey of magnetic cooling work for the scientifically trained nonspecialist.

J. W. STOUT

UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

## ● QUANTITATIVE ORGANIC ANALYSIS VIA FUNCTIONAL GROUPS

***Sidney Siggia*, Research Analyst, General Aniline and Film Corporation. Second edition. John Wiley & Sons, Inc., New York, 1954. x + 227 pp. 14 × 22 cm. $5.**

THE author states his case very clearly in the preface: "... the first edition of this book was out of date before it appeared. It is the purpose of this second edition to bring the subject up to date as far as possible."

Included among the new procedures are nonaqueous titrations for enols, acids, imides, anhydrides, acid chlorides, single amines, mixtures of amines, quaternary ammonium compounds, sulfonamides, and oxirane oxygen. The section on carbonyl groups has a gravimetric method as well as silver ion oxidation and Schiff base formation techniques for aldehydes. Other noteworthy additions include applications of phase diagrams in analysis, an excellent discussion of the techniques and reasoning used in developing new methods, and some examples of the use of quantitative data to identify substances.

The second edition will be more useful to research workers than the first edition. The application to instructional use is obvious.

The typography is good and there are only a few minor errors.

K. G. STONE

MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

★ ★

# Out of the Editor's Basket

### Ultraviolet Monochromatic Illuminator

The new Farrand UV Monochromatic Illuminator is small, compact, and convenient to use with microscopes, colorimeters, photometers, and similar instruments.

It is designed to yield monochromatic illumination at any chosen wave length between 220 and 440 millimicrons.

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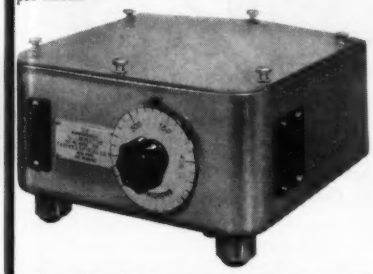

The Illuminator can be set up with auxiliary equipment for making transmission, absorption, emission, radiation, reflection, fluorescence, and phosphorescence measurements or used for irradiation purposes.

Complete details are given in Bulletin 811 which is available from Farrand Optical Co., Inc., Bronx Blvd. and E. 238th St., New York 70, New York.

### Conversion Factors for U. S. Units of Measure

The New York Laboratory Supply Company, Inc., has just published a 32-page booklet, No. 101, "U. S. Units of Measure and Conversion Factors." The booklet is unique in giving reciprocal conversions in adjacent columns of a single table, thus eliminating the need for searching in two separate places. Three Graphic Temperature Conversion charts (degrees Centrigrade versus degrees Fahrenheit) are given, in which the scale divisions and ranges are respectively: 0.1° from −10° to +120°C., 1° from −100° to +500°C., and 10° from absolute zero to +5,500°C. In addition to a thorough treatment of all the more scientific units encountered in practical work, the booklet also contains such useful tables as Wire and Sheet Gage Numbers, Screw Threads, Drill Sizes, and the RTMA Color Code for Resistors and Condensers.

Because of its limited edition, copies of this useful little handbook will be supplied only to interested technical personnel writing in on their company or institution letterhead to: New York Laboratory Supply Co., Inc., 76 Varick St., New York 13, New York.

### New Beckman Spectrophotometer

Beckman has announced a new ultraviolet near-infrared spectrophotometer. This is the first commercially available instrument designed specifically for the near-infrared region of the spectrum—filling an important gap in spectrochemical analysis. Its lead sulfide detector and quartz monochromator permit high-speed transmittance recording at cost and performance unmatched by conventional infrared instruments. Using a photomultiplier detector for ultraviolet work, the new instrument offers a guaranteed wave-length range of 220 to 2700 mμ.

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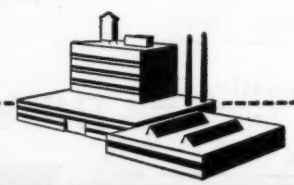

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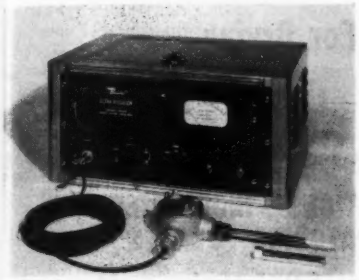
**Bendix Ultra-Viscoson**

The Cincinnati Division of the Bendix Aviation Corp. has made some important advancements in its new viscosity measuring instrument, the Bendix Ultra-Viscoson. This instrument, utilizing ultrasonic principles, is now offered in a complete line of indicating, recording, and control systems for industrial and laboratory use.



The versatility of these systems can be emphasized by the fact that they are presently being employed to control fuel-oil blending, fractionation of lubricating oils, asphalt oxidation, and asphalt cutback in petroleum refineries and fuel atomization in conjunction with open-hearth furnaces in the steel industry. Success has also been achieved with laminating resins, gravure inks, and interface detection.

A folder describing the instrument in detail is available from Bendix Aviation Corp., 203 W. Third St., Cincinnati 2, Ohio.

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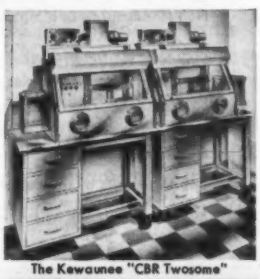

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**References**

(1) Ind. Eng. Chem. 25-653 (June, 1933)

(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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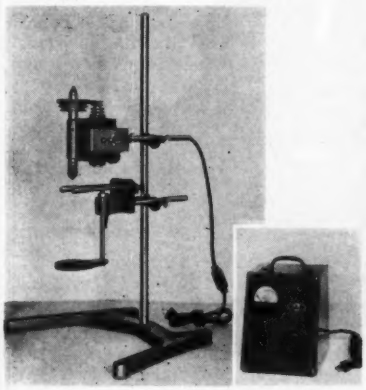

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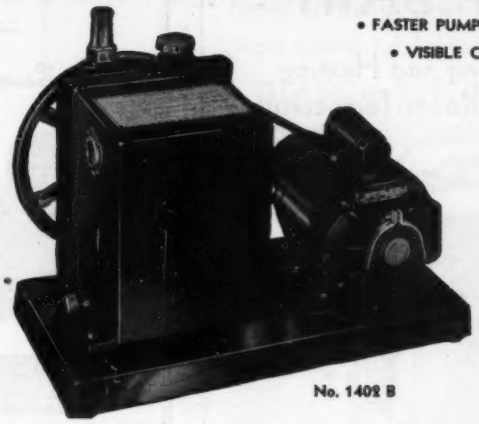

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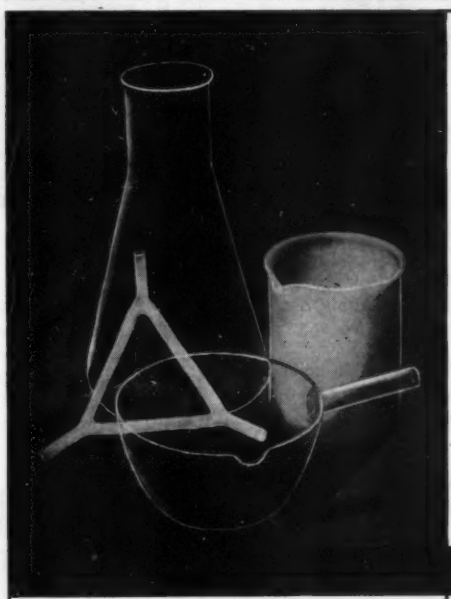

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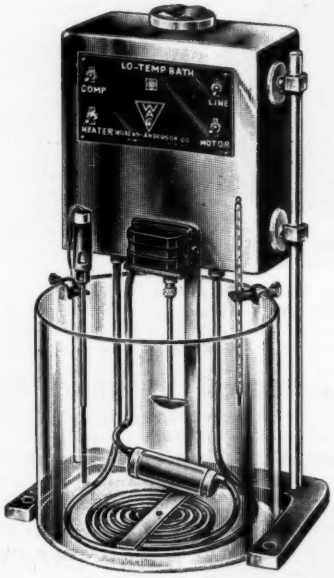


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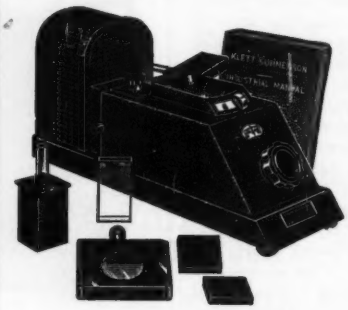

*Photoelectric Glass Cell Colorimeter*

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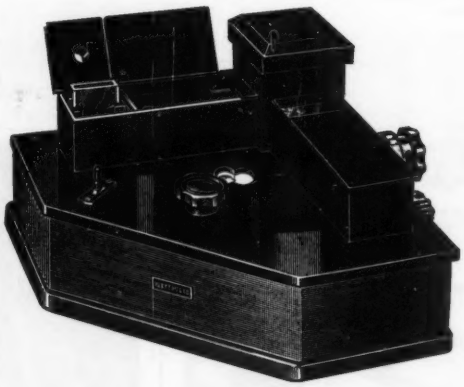
***The Klett Fluorimeter***



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for the rapid, nondestructive chemical analysis of metals, powders, and liquids.

Previous machines of this type used the phenomenon of the fluorescence of materials when exposed to X-rays and the analysis of this fluoresence to determine the amount of each material present in the sample. The new curved crystal spectrometer has increased sensitivity, precision, and speed of analysis to such an extent that the usefulness of the X-ray method has been greatly extended, the manufacturer claims.

Previous equipment of this type, using the restricting flat crystal, was limited to one channel (the analysis of one element at a time). The new XIQ, by using the techniques developed from other types of Spectrography, permits multichannel work or the simultaneous analyses of many elements...as many as eight at one time.

Another advantage of this equipment is found in the recording console. This unit records the exact percentage of elements found in the sample being analyzed and produces this information automatically on inked graphs in less than two minutes.

Complete technical information on this new equipment is available from the manufacturer.

**Leeuwenhoek Keepsake**

"The Discovery of Unicellular Life," excerpts from communications by Antoni van Leeuwenhoek to the Royal Society of London, is a reprint from the "Collected Letters of Antoni van Leeuwenhoek," Vols. 1 and 2 (1939 and 1941), published by Messrs. Swets & Zeitlinger, Ltd., Amsterdam. This little pamphlet is a keepsake issued by the editors of *Chronica Botanica* at the occasion of the dedication of the Institute of Microbiology, Rutgers University, June, 1954. Copies are available, without charge, from The Chronica Botanica Co., Waltham 54, Massachusetts.

**Karl Fischer Reagent**

Fisher Scientific Co., 717 Forbes St., Pittsburgh 19, Pennsylvania announces a new stabilized single-solution Karl Fischer reagent, which is said to maintain its titer within convenient working limits for at least a year, yielding sharp and stable end points in electrometric titrations. Catalogue number is So-K-3.

**Pressure Balance**

Consolidated Engineering Corp., 300 N. Sierra Madre Villa, Pasadena 8, California, has recently released its new Precision Pressure Balance, Type 37-103. This instrument allows fast, accurate, nonmanual measurement of precision pressures; a visual, digital readout counter with digits to 1000 makes immediate readings possible. It is designed so that readings may be held when required or attached to electrical tabulating devices through a built-in electrical analog d.-c. output of 10 volts.

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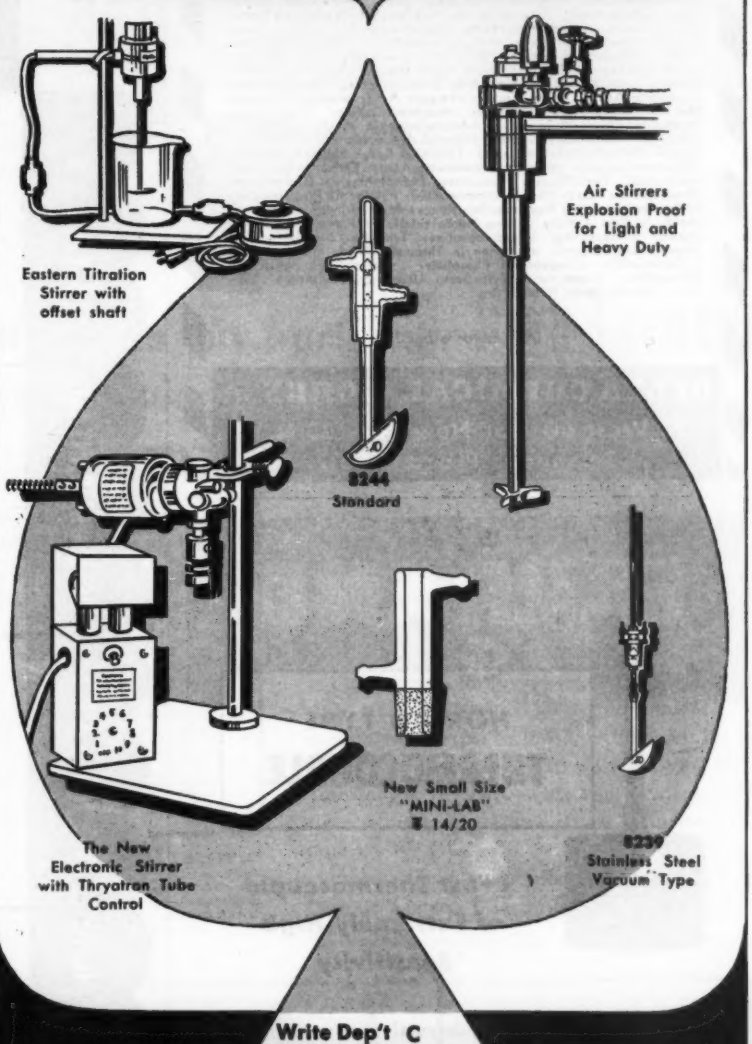
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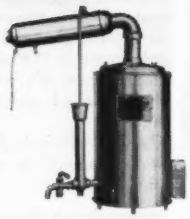

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Illium, samarskite, $C_{28}H_{56}$, and albite-microcline are available from the Research & Control Instruments Division, North American Philips Co. Inc., 750 S. Fulton Ave., Mount Vernon, New York.

The Illium and samarskite specimens were analyzed for elements on the X-ray spectrograph. The Illium chart shows the presence of molybdenum, tungsten, copper, nickel, cobalt, iron, manganese, and chromium. The samarskite chart shows iron, zinc, yttrium, zirconium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium, thulium, ytterbium, hafnium, lead, bismuth, thorium, and uranium.

The $C_{28}H_{56}$ and albite-microcline charts were analyzed on the X-ray diffractometer. The $C_{28}H_{56}$ chart shows the extremely sharp, strong, and nearly equally spaced reflections down to low angles for this pure hydrocarbon. The albite-microcline chart shows three conditions: albite alone, microcline alone, and a 50% mixture of each.

### Germanium Reagent

The Jasonols Chemical Corp., 825 E. 42nd St., Brooklyn 10, New York, announces the availability of phenylfluorone, a sensitive and selective reagent for the determination of germanium.

Since the organic compounds of germanium will continue to increase in number and commercial availability the use of phenylfluorone for determining germanium colorimetrically will aid the germanium chemist in developing many useful products.

### New Literature

● Will Corp. has just published a new 196-page Laboratory Reagents Catalog (C-6) with prices current to Sept. 1, including the new Eastman Organic Chemicals listings of Aug. 16.

Organics and inorganics are alphabetically arranged in separate sections. Grouped also for convenience are Stains, Indicators, Sugars, Diagnostic Reagents, Culture Media, and Histological Agents—many not listed in any other source.

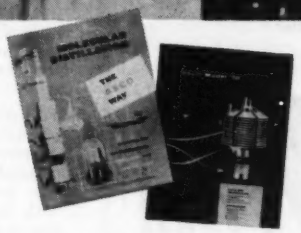
Listings are brief but complete and include synonyms and commonly-used terms. The catalog contains over 6000 items fully indexed and with many helpful cross-references.

For your free copy write Will Corp., Rochester 3, New York.

● A new bulletin just published by the Climax Molybdenum Co., 500 Fifth Ave., New York 36, New York, is intended as a guide to the selection of molybdenum products for applications in the chemical process industries. It describes briefly the commercially available products, their manufacture and their principal uses. This bulletin is available without charge.

● A new edition of General Bulletin No. 100 is now available from Photovolt Corp., 95 Madison Ave., New York 16, New York. The bulletin contains descriptions and illustrations of their complete line of photoelectric and electronic measuring instruments.

● Association Films, national distributor of 16-mm. sound motion pictures, announces publication of its 40th annual film catalog, "Selected Motion Pictures."



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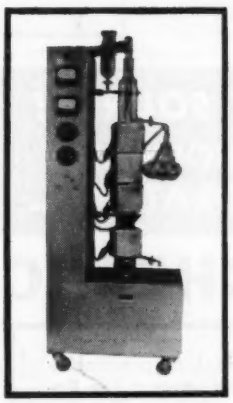

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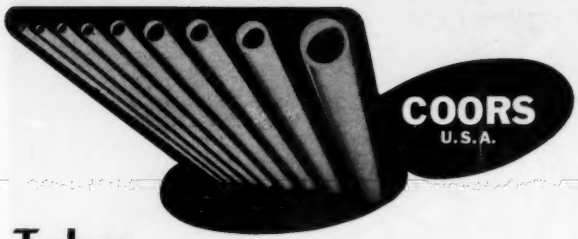


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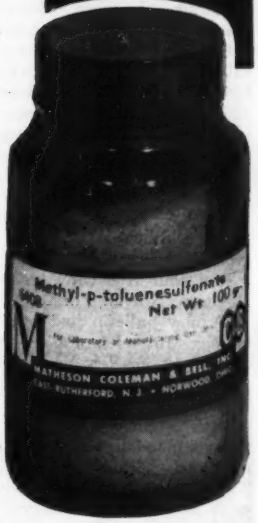


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● The American Iron and Steel Institute, 350 Fifth Ave., New York 1, New York, announces the publication of "A Teachers Guide to Industry-Produced Reference and Audio-Visual Materials on Iron and Steel." This is a bibliography of films, filmstrips, books, and charts about the iron and steel industry, with a short description of each item listed and suggestions on grade levels and subject matter areas in which it might be useful. The American Iron and Steel Institute will supply a free copy of the booklet on request.

● A technical bulletin giving the more important organic reactions of succinonitrile has been compiled from a bibliography of 72 references by Monsanto Chemical Co.'s Organic Chemicals Division.

The reactions, which are summarized in a two-page diagram with text references, include those of both the nitrile and methylene groups. The bulletin also contains suggested uses for succinonitrile and provides toxicity and handling information. This is Monsanto Technical Bulletin No. O-116, and is available from the Public Relations Department, Monsanto Chemical Co., 1700 S. Second St., St. Louis 4, Missouri.

**New Literature**

● A new technical booklet that includes a wide range of data relative to the use of Vinsol resin as a low-cost component of Buna-N, vinyl, and other type adhesives is now available from Hercules Powder Co., Wilmington 99, Delaware.

Vinsol resin is a hard, brittle, high-melting thermoplastic material derived from southern pine wood. The excellent compatibility of Vinsol with a wide variety of resins and film-formers, plus its low price, makes it an important component in many types of adhesive compositions.

Product applications discussed are divided into two sections. One is titled rubber-base adhesives and the other includes information about the use of Vinsol in vinyl resin adhesives, and adhesives based on styrene, phenol, urea-starch, cellulose, and polymerized oil.

● The Carborundum Metals Co., Inc., Akron, New York, has recently published a booklet on "Facts About Zirconium" for general distribution. This is a concise compilation of information about the history and production of zirconium. The mechanical and physical properties, chemical properties, and facts about fabrication of zirconium, such as melting, forging, rolling, welding, and machinability, are discussed. One chapter treats of zirconium chemicals such as zirconium tetrachloride, dioxide, sulfate, and Carbo-Cast-Aid.

The appendix lists data on crystallographic features, atomic and nuclear properties, etc. Copies are available from the Public Relations Department, The Carborundum Co., Niagara Falls, N. Y.


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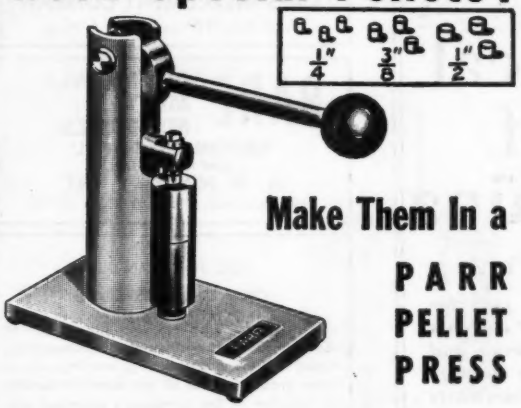


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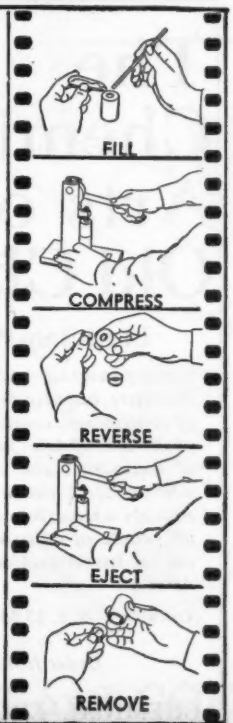


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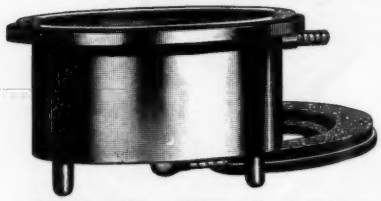

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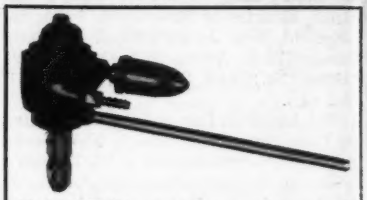

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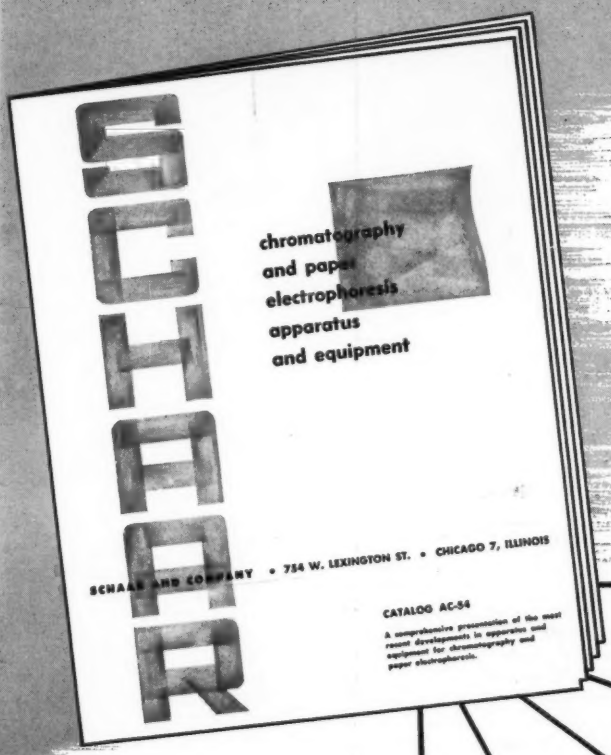
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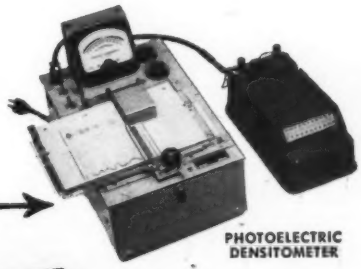

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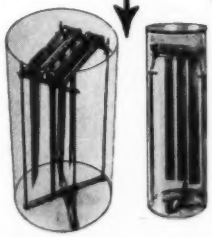

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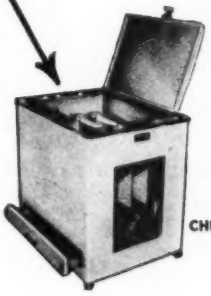

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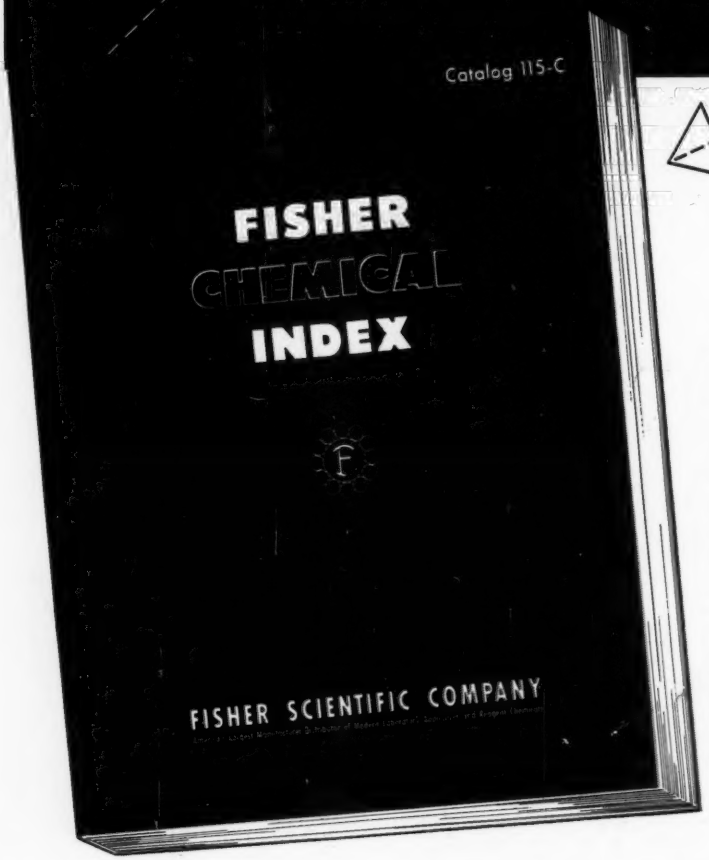


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